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16. ABSTRACT The report gives results of a study of the capabilities of refrigeration systems, operated at three temperatures, to control volatile organic compound (VOC) emissions from truck loading at bulk gasoline terminals. Achievable VOC emission rates were calculated for refrigeration systems cooling various gasoline/air mixtures to -62 C, -73 C, and -84 C by estimating vapor/liquid equilibrium compositions for VOC/air mixtures. Emission rates were calculated for inlet streams containing vapors from low- and high-volatility gasolines at concentrations of 15, 30, and 50% by volume (22.5, 45, and 75% measured as propane). Predicted VOC emission rates for systems cooling various inlet streams to -62 C ranged from 48 to 59 mg VOC/liter of gasoline loaded. Predicted VOC were 21 to 28 mg/l loaded for systems operating at -73 C and 8.7 to 12 mg/l loaded for systems operating at -84 C. Compressor electrical requirements and relative capital costs for systems operating at the above temperatures were estimated for model systems using the results of a computer simulation. Compressor electrical requirements ranged from 0.11 to 0.45 Whr/l loaded, depending on the inlet VOC concentration and the outlet temperature. The capital cost to build a system designed to cool vapors to -84 C is estimated to be about 9% higher than for a system designed to operate at -73 C.

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ABSTRACT

The capabilities of refrigeration systems operated at three temperatures to control volatile organic compound (VOC) emissions from truck loading at bulk gasoline terminals were investigated in this study. Electricity requirements and relative costs associated with systems operating at each temperature were calculated.

Achievable VOC emission rates were calculated for refrigeration systems cooling various gasoline/air mixtures to temperatures of -62°C (-80°F), -73°C (-100°F), and -84°C (-120°F) by estimating vapor-liquid equilibrium compositions for VOC/air mixtures. Equilibrium compositions were estimated using a computer simulation program and the Soave-Redlich-Kwong and Peng-Robinson methods of predicting thermodynamic properties of mixtures. Emission rates were calculated for inlet streams containing vapors from low volatility and high volatility gasolines, at concentrations of 15, 30, and 50 percent by volume (22.5, 45, and 75 percent measured as propane). Predicted VOC emission rates for systems cooling various inlet streams to -62°C ranged from 48 to 59 mg VOC/liter of gasoline loaded. Predicted VOC emissions were 21 to 28 mg/ℓ loaded for systems operating at -73°C and 8.7 to 12 mg/ℓ loaded for systems operating at -84°C.

Compressor electrical requirements and relative capital costs for systems operating at the above temperatures were estimated for model systems using the results of the computer simulation. Compressor electricity requirements ranged from 0.11 to 0.45 Whr/ℓ loaded depending upon the inlet VOC concentration and the outlet temperature. The electricity requirement to cool vapors to -84°C was estimated to be 54 to 77 percent greater than the requirement to cool vapors to -62°C, depending on the organic content of the inlet stream. The electricity requirement to cool vapors to -73°C is estimated to be 23 to 36 percent greater than that to cool vapors to -62°C . The capital cost to build a system designed to cool vapors to -84°C is estimated to be about 9 percent higher than the capital cost to build a system designed to operate at -73°C, which is estimated to be about 12 percent higher than the cost to build a system designed to operate at -62°C.

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SECTION 1

SUMMARY

The primary objective of this study was to investigate the capabilities of refrigeration systems operated at various temperatures to control volatile organic compound (VOC) emissions from truck loading at bulk gasoline terminals. In addition, the electricity requirements and relative costs of systems operating at various temperatures were calculated.

VOC emissions from bulk gasoline terminals result from the displacement of gasoline laden vapors from trucks during truck loading. These emissions are generally controlled by ducting the displaced vapor - a mixture of air and hydrocarbons - to a system which removes the hydrocarbons. Refrigeration is one of the techniques which can be used to control these emissions. In refrigeration control systems, displaced vapors laden with gasoline vapors are cooled to cryogenic temperatures (-46°C to -84°C or -50°F to -120°F) in order to condense the gasoline vapors.

Achievable VOC emission rates were calculated for refrigeration systems cooling various gasoline vapor/air mixtures to temperatures of -62°C (-80°F), -73°C (-100°F), and -84°C (-120°F). The control systems studied would first cool the mixtures to 4.4°C (40°F) in a precooler in order to remove most of the moisture present. Vapors from the precooler would then be cooled to -62°C, -73°C, or -84°C in the main condenser. Calculations of emission rates were performed for inlet streams containing vapors from low volatility and high volatility gasolines, at concentrations of 15, 30, and 50 percent by volume (22.5, 45, and 75 percent measured as propane). All of the inlet streams studied were at 60 percent relative humidity.

The achievable emission rates were calculated by estimating vapor-liquid equilibrium compositions for VOC/air mixtures at the above temperatures. Equilibrium compositions were estimated using a computer simulation program and the Soave-Redlich-Kwong and Peng-Robinson methods of predicting thermodynamic properties of mixtures.

Compressor electrical requirements were estimated for systems designed to cool these inlet streams to the three outlet temperatures. Relative capital and energy costs were estimated for systems designed to cool an inlet stream containing 30 percent VOC by volume to -62°C, -73°C and -84°C.

Figures 1 and 2 illustrate the dependence of VOC emissions on condenser outlet temperature for various inlet streams. The values presented for VOC emissions include all gasoline vapor components except methane and ethane. Methane and ethane are not considered VOC for the purposes of Environmental Protection Agency regulations. Figure 3 illustrates the relationship between

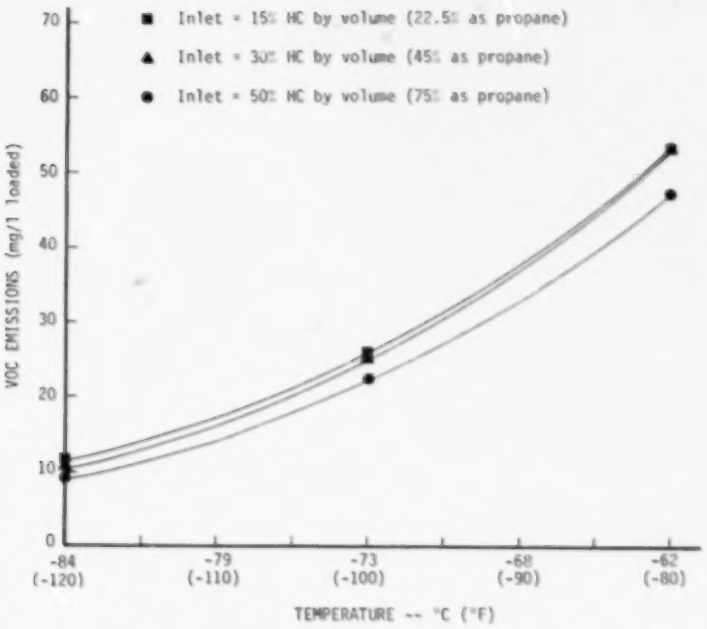

Figure 1. Effect of condenser outlet temperature on VOC emissions -- low volatility vapors.

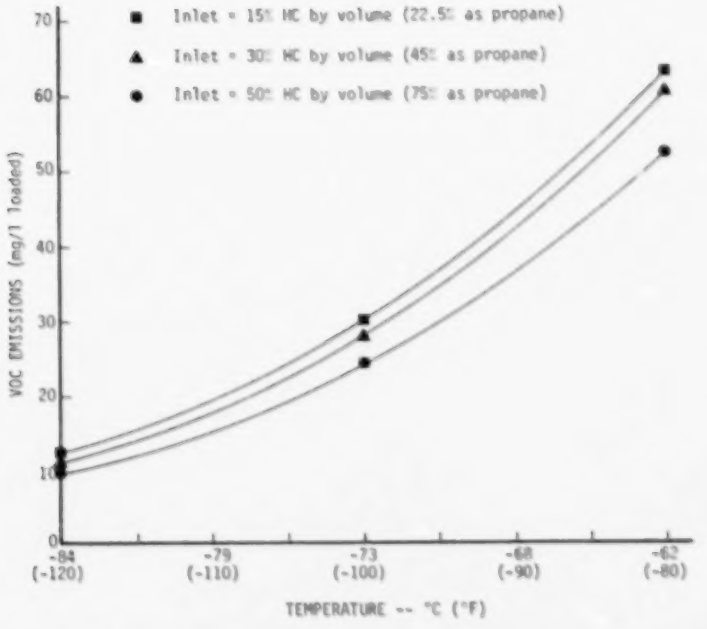

Figure 2. Effect of condenser outlet temperature on VOC emissions -- high volatility vapors.

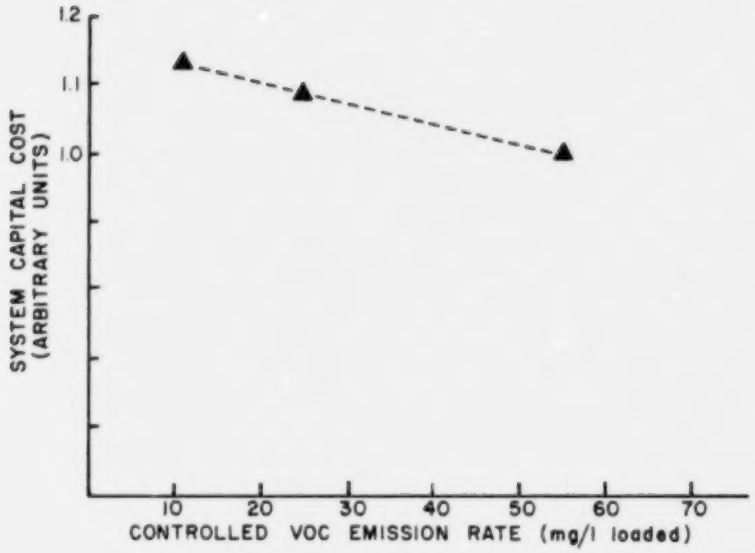

Figure 3. Variation of system capital cost with controlled VOC emission rate for systems designed to cool VOC/air mixtures containing 30 percent VOC by volume to temperatures of -62°C, -73°C, and -84°C at a maximum flow rate of 14,000 ℓ/min.

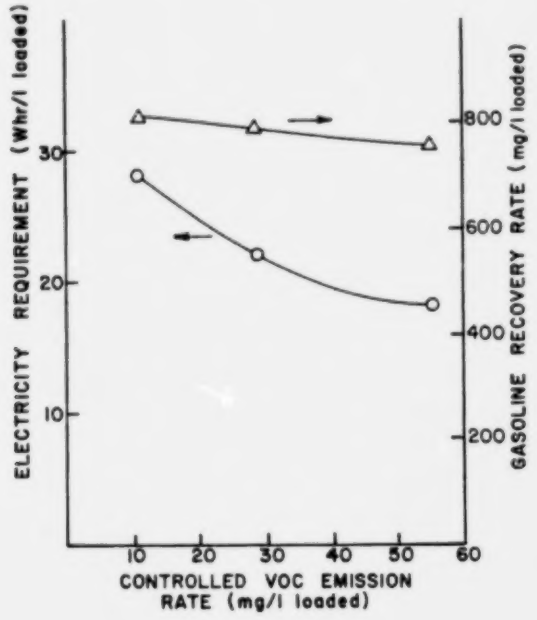

Figure 4. Variation of system electricity requirements and gasoline recovery rate with controlled VOC emission rate for systems designed to cool VOC/air mixtures containing 30 percent VOC by volume to temperatures of -62°C, -73°C, and -84°C at a maximum flow rate of 14,000 ℓ/min.

refrigeration system capital cost and the controlled VOC emission level, while Figure 4 illustrates the variation of the system electricity requirement and gasoline recovery rate with the controlled VOC emission level, for a system designed to handle inlet vapors containing 30 percent by volume VOC at a maximum flow rate of 14,000 ℓ/min.

SECTION 2

INTRODUCTION

Federal New Source Performance Standards (NSPS) were recently proposed which would limit volatile organic compound (VOC) emissions from new facilities at bulk gasoline loading terminals.[1,2] The proposed standards would limit VOC emissions from vapor collection systems, which remove gasoline vapors from air displaced during truck loading, to 35 mg/ℓ. For the purpose of the NSPS, VOC means "any organic compound which participates in atmospheric photochemical reactions." Except for methane and ethane, all of the compounds generally present in gasoline vapors are considered VOC.[3] VOC emissions from most bulk gasoline terminals are currently limited by State Implementation Plan (SIP) regulations, which typically require that emissions from vapor collection systems be less than 80 mg/ℓ of gasoline loaded.[2]

Table 1 lists the organic compounds which have been detected in vapors displaced during gasoline loading, and the relative abundances of these compounds in vapors from high and low volatility gasolines.[4,5] High volatility gasoline is generally loaded in the winter, while low volatility gasoline is generally loaded in the summer. It should be noted that the abundances of specific compounds in gasoline vapor in a vapor/air mixture varies with the temperature and the amount of air present; however, test data are not available to quantify the extent to which the relative abundances would vary.

A number of techniques have been used to control emissions from gasoline loading. These control techniques include carbon adsorption, incineration, refrigeration, compression-refrigeration-absorption, compression-refrigeration-condensation, and lean oil absorption. With the exception of incineration, all of the above control systems also recover gasoline.

The primary purpose of this study was to determine theoretically the minimum effluent organic concentrations that can be attained by refrigeration of gasoline vapor/air mixtures to various temperatures. A secondary purpose was to estimate the electricity requirements and costs of refrigeration control systems operating at various temperatures and thus to estimate the relative costs and electricity requirements to achieve various levels of control.

In this report, the theoretical control capabilities, power requirements, and relative costs are estimated for refrigeration control systems. In refrigeration control systems, air streams laden with gasoline vapors are cooled to cryogenic temperatures in order to condense the gasoline vapors. Refrigeration systems

TABLE 1. BREAKDOWN OF HC COMPONENTS OF HIGH AND LOW VOLATILITY GASOLINE VAPORS[4,5]

Component	Low volatility Mole percent	High volatility Mole percent
Methane (C_1)	2.68	1.31
Ethane (C_2)	0.46	0.31
Propane (C_3)	1.83	1.76
Iso-Butane (C_4)	13.87	11.45
N-Butane (C_4)	29.09	44.35
2-Butene (C_4)	5.24	0.24
3-Methyl-1-Butene (C_5)	--	0.26
Iso-Pentane (C_5)	15.56	19.83
N-Pentane (C_5)	10.47	9.62
N-Pentene (C_5)	4.09	1.10
2-Methyl-2-Butene (C_5)	0.61	1.54
2,2-Dimethylbutane (C_6)	--	0.39
N-Hexane (C_6)	2.07	1.34
2-Methylpentane (C_6)	4.58	2.89
Cyclopentane (C_6)	0.37	--
3-Methylpentane (C_6)	2.33	--
Methylcyclopentane (C_6)	1.28	0.70
Benzene (C_6)	0.90	0.46
Cyclohexane (C_6)	0.98	--
Saturated Heptane (C_7)	1.92	0.78
Toluene (C_7)	1.26	0.70
M,P-Xylene (C_8)	0.28	0.18
O-Xylene (C_8)	0.07	0.06
Saturated Octane (C_8)	0.06	0.73

currently in use to control gasoline vapor emissions operate at temperatures between -46°C (-50°F) and -84°C (-120°F). Emissions from refrigeration systems tested during the development of background information for the NSPS ranged from 30 to 130 mg/liter of vapor entering the refrigeration control system. For loading of a vapor-tight truck, the volume of vapor entering the control system would be approximately equal to the volume of gasoline loaded.

Achievable VOC emission rates were calculated for refrigeration systems cooling various gasoline vapor/air mixtures to temperatures of -62°C, -73°C, and -84°C. The control systems studied would first cool the mixtures to 4.4°C (40°F) in a precooler in order to remove most of the moisture present. Vapors from the precooler would then be cooled to -62°C, -73°C, or -84°C in the main condenser (Figure 5). Calculations of emission rates were performed for inlet streams containing low volatility and high volatility gasoline vapors in concentrations of 15, 30, and 50 percent by volume (22.5, 45, and 75 percent measured as propane). All of the inlet streams studied were at 60 percent relative humidity.

Compressor electrical requirements were estimated for systems designed to cool these inlet streams to the three outlet temperatures. Relative capital and energy costs were estimated for systems designed to cool an inlet stream containing 30 percent VOC by volume to -62°C, -73°C and -84°C.

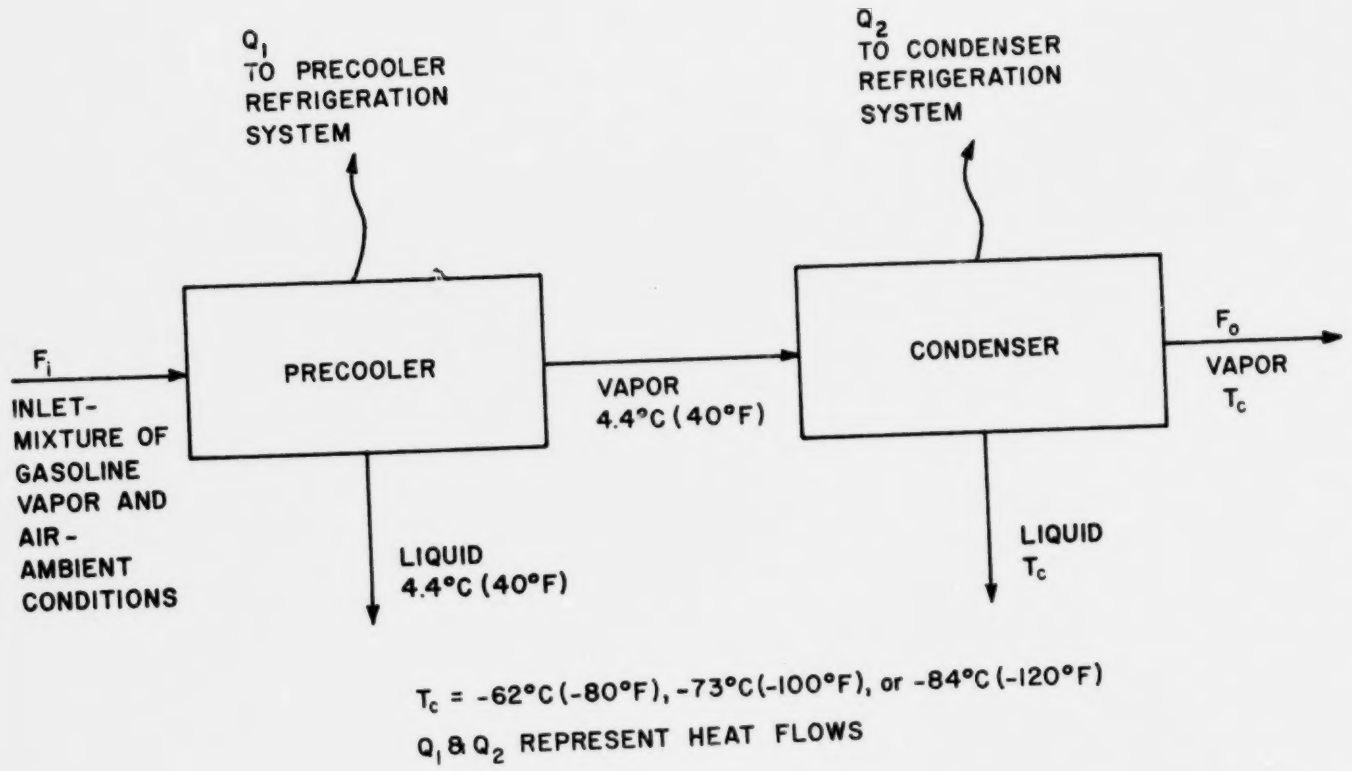

Figure 5. Vapor flow in the refrigeration systems studied.

SECTION 3

ACHIEVABLE EMISSION RATES

The emission rate for a refrigeration system controlling a bulk gasoline terminal can be estimated from the refrigeration system inlet flow rate and the concentrations of VOCs in the main condenser outlet stream by the following equation:

$$ER = \frac{M\sigma}{F} \sum_j MW_j c_j$$

where ER = the emission rate in g/ℓ of gasoline loaded. The volume of gasoline loaded is assumed to be equal to the volume of vapor entering the refrigeration system,

$M\sigma$ = the flow rate of vapors out of the refrigeration system in g-moles/sec (Figure 5),

F = the flow rate of vapors into the refrigeration system in ℓ/sec (Figure 5),

c_j = the concentration of VOC compound j in the condenser outlet stream (Figure 5) in g-moles/total g-moles.

MW_j = the molecular weight of VOC compound j in g/g-mole.

The lowest achievable emission rate for refrigeration to a given temperature occurs when the refrigeration system is designed so that the vapor stream leaving the main condenser is at thermodynamic equilibrium with the liquid stream leaving the condenser (Figure 5). Thus, the lowest achievable emission rate for refrigeration to a given temperature can be calculated by determining the composition of the vapor phase which would result from the cooling of the VOC/air mixture entering the main condenser to the condenser operating temperature.

Vapor/liquid equilibrium compositions were calculated for precooler inlet streams containing high volatility gasoline vapors and low volatility gasoline vapors (Table 1) in concentrations of 15, 30 and 50 percent by volume cooled to -62°C, -73°C and -84°C. Inlet streams were assumed to have relative humidities of 60 percent. The relative humidity would not impact the emission rate achievable by refrigeration to a given temperature, but would have a small effect on the heat removal requirement to achieve the desired temperature.

A computer simulation program was used to estimate equilibrium compositions of the liquid and vapor streams resulting from the cooling of VOC/air mixtures to cryogenic temperatures. The program was developed by Simulation Sciences,

Inc.*, and the use of the program was arranged through the McDonnell Douglas Automation Company.+ A number of methods are commonly used to estimate thermodynamic property values using measured values at benchmark conditions. These methods include the Soave-Redlich-Kwong method, the Peng-Robinson method, the Benedict-Webb-Rubin method, the Redlich-Kwong method, and the Chao-Seader method. These methods and their relative merits are discussed briefly in Appendix A.

The Soave-Relich-Kwong (SRK) method was chosen to estimate equilibrium vaporization factors (K values) and enthalpy values for the various mixture components under various conditions. The Peng-Robinson (PR) method was used to estimate liquid densities. These methods were chosen because of their accuracy in the cryogenic range. Both of these methods are accurate for pressures up to about 35,000 kPa (5,000 psia) and over the temperature range -155 to +260°C (-250 to + 500°F).

Predicted equilibrium compositions of condenser outlet vapor streams for various condenser operating temperatures and inlet streams are presented in Tables 2 and 3. Table 2 presents predicted outlet compositions for inlet streams containing low volatility vapors, while Table 3 presents predicted outlet compositions for inlet streams containing high volatility vapors. The predicted compositions presented in these tables were derived by simulating the cooling of mixtures of air and high and low volatility gasoline vapors as shown in Figure 5, with the vapor first cooled to 4.4°C and then to a final temperature of -62°C, -73°C or -84°C. Inlet VOC/air mixtures containing 15, 30, and 50 percent by volume high or low volatility gasoline vapors were studied. The simulations were performed using the measured high and low volatility gasoline vapor compositions presented in Table 1.

Table 4 presents total hydrocarbon and VOC (hydrocarbons excluding methane and ethane) emission rates derived from the condenser vapor outlet composition data presented in Tables 2 and 3. Emission reductions are also presented. The emission rates and reductions are expressed in terms of mass per unit volume of gasoline loaded. As noted earlier the volume of gasoline loaded is approximately equal to the volume flow of air into the control system.

The potential errors of the emission values presented in Table 4 can be estimated from reported potential errors in K values predicted by the SRK method. Reported errors in K values predicted by the SRK method for the components in gasoline vapors range from about 3 percent for iso-butene to about 29 percent for benzene.[6] Because the predicted equilibrium concentration of a compound in the vapor phase is directly proportional to its K value (see Appendix A), the potential error in a prediction of total hydrocarbon emissions can be estimated by taking an average of the K value errors for emitted compounds weighted by the vapor phase concentration of the compounds. The potential error of the values presented in Table 4 has been estimated at about ± 10 percent.

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TABLE 2. COMPONENT SPECIFIC BREAKDOWN OF CONDENSER OUTLET STREAMS FOR LOW VOLATILITY INLET VAPORS COOLED TO VARIOUS TEMPERATURES (ppm by moles)

	15% HC inlet			30% HC inlet			50% HC inlet		
	-62°C (-80°F)	-73°C (-100°F)	-84°C (-120°F)	-62°C (-80°F)	-73°C (-100°F)	-84°C (-120°F)	-62°C (-80°F)	-73°C (-100°F)	-84°C (-120°F)
Methane (C_1)	4,360	4,690	4,720	10,900	10,900	11,200	25,100	25,600	25,800
Ethane (C_2)	763	750	713	1,710	1,600	1,480	3,610	3,320	2,830
Propane (C_3)	2,250	1,740	1,130	3,850	2,570	1,510	6,050	3,770	2,020
Iso-Butane (C_4)	8,710	4,770	2,210	11,000	5,460	2,450	13,800	6,730	2,920
N-Butane (C_4)	10,800	5,050	2,040	12,500	5,520	2,240	14,600	6,490	2,570
2-Butene (C_4)	1,560	693	268	1,780	761	298	2,060	886	340
3-Methyl-1-butene (C_5)	0	0	0	0	0	0	0	0	0
Iso-Pentane (C_5)	1,480	555	187	1,490	557	193	1,440	553	189
N-Pentane (C_5)	590	209	65.9	582	206	67.2	523	190	61
N-Pentene (C_5)	199	67.1	20.3	198	67.4	21.1	179	62.7	19.4
2-Methyl-2-Butene (C_5)	28.3	9.7	3.0	28.0	9.7	3.1	24.6	8.8	2.8
2,2-Dimethylbutane (C_6)	0	0	0	0	0	0	0	0	0
N-Hexane (C_6)	16.5	4.9	1.3	13.4	4.0	1.1	7.5	2.3	0.6
2-Methylpentane (C_6)	64.9	20.1	5.6	56.2	17.7	5.1	36.3	11.8	3.4
Cyclopentane (C_6)	11.3	3.8	1.2	11.3	3.9	1.2	9.3	3.3	1.0
3-Methylpentane (C_6)	26.7	8.2	2.2	22.9	7.1	2.0	14.1	4.5	1.3
Methylcyclopentane (C_6)	9.6	2.9	0.8	8.1	2.5	0.7	4.5	1.4	0.4
Benzene (C_6)	5.2	1.5	0.4	4.5	1.4	0.4	2.5	0.8	0.2
Cyclohexane (C_6)	5.0	1.5	0.4	4.0	1.2	0.3	2.0	0.6	0.2
Saturated Heptane (C_7)	4.3	1.1	0.3	2.7	0.7	0.2	1.0	0.3	<0.1
Toluene (C_7)	0.8	0.2	<0.1	0.4	<0.1	<0.1	0.1	<0.1	<0.1
M,P-Xylene (C_8)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0	0
O-Xylene (C_8)	<0.1	<0.1	<0.1	<0.1	<0.1	0	0	0	0
Saturated Octane (C_8)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Air	968,000	981,000	989,000	956,000	955,000	981,000	932,000	952,000	963,000
H_2O	749	272	87.3	382	139	46.5	189	70.8	23.5
Total Hydrocarbon ppm as Propane	104,000	57,800	22,900	125,000	59,100	26,000	151,000	71,900	30,800

TABLE 3. COMPONENT SPECIFIC BREAKDOWN OF CONDENSER OUTLET STREAMS FOR HIGH VOLATILITY INLET VAPORS COOLED TO VARIOUS TEMPERATURES (ppm by moles)

	15% HC inlet			30% HC inlet			50% HC inlet		
	-62°C (-80°F)	-73°C (-100°F)	-84°C (-120°F)	-62°C (-80°F)	-73°C (-100°F)	-84°C (-120°F)	-62°C (-80°F)	-73°C (-100°F)	-84°C (-120°F)
Methane (C_1)	2,260	2,300	2,310	5,370	5,460	5,500	12,500	12,700	12,800
Ethane (C_2)	514	505	480	1,150	1,090	981	2,390	2,160	1,800
Propane (C_3)	2,160	1,660	1,080	3,580	2,400	1,370	5,240	3,190	1,690
Iso-Butane (C_4)	7,140	3,870	1,780	8,580	4,310	1,900	10,000	4,850	2,100
N-Butane (C_4)	16,500	7,610	3,060	18,000	8,080	3,210	19,800	8,800	3,490
2-Butene (C_4)	71.8	31.5	12.2	77.9	33.7	13.0	84.8	36.6	14.1
3-Methyl-1-Butene (C_5)	31.2	11.8	4.0	31.0	12.0	4.2	31.0	12.1	4.2
Iso-Pentane (C_5)	1,880	695	233	1,830	695	237	1,770	683	234
N-Pentane (C_5)	543	189	59.4	523	188	60.4	484	177	57.2
N-Pentene (C_5)	53.5	17.9	5.4	52.3	18.1	5.6	48.6	17.2	5.3
2-Methyl-2-Butene (C_5)	71.5	24.3	7.5	70.0	24.7	7.8	64.0	23.0	7.3
2,2,-Dimethylbutane (C_6)	12.3	4.1	1.3	11.5	4.0	1.2	9.5	3.4	1.1
N-Hexane (C_6)	10.6	3.1	0.8	9.6	2.9	0.8	6.2	1.9	0.5
2-Methylpentane (C_6)	40.5	12.4	3.4	37.3	11.9	3.4	27.2	8.9	2.5
Cyclopentane (C_6)	0	0	0	0	0	0	0	0	0
3-Methylpentane (C_6)	0	0	0	0	0	0	0	0	0
Methylcyclopentane (C_6)	5.3	1.6	0.4	5.1	1.6	0.4	3.3	1.0	0.3
Benzene (C_6)	2.8	0.8	0.2	2.8	0.8	0.2	1.7	0.5	0.1
Cyclohexane (C_6)	0	0	0	0	0	0	0	0	0
Saturated Heptane (C_7)	1.7	0.5	0.1	1.5	0.4	0.1	0.6	0.2	<0.1
Toluene (C_7)	0.5	0.1	<0.1	0.4	0.1	<0.1	0.1	<0.1	<0.1
M,P-Xylene (C_8)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0	0
O-Xylene (C_8)	<0.1	<0.1	<0.1	<0.1	<0.1	0	<0.1	0	0
Saturated Octane (C_8)	0.5	0.1	<0.1	0.4	0.1	<0.1	0.1	<0.1	<0.1
Air	968,000	983,000	991,000	960,000	978,000	987,000	947,000	967,000	978,000
H_2O	794	287	92.0	384	143	46.9	184	69.1	23.0
Total Hydrocarbon ppm as Propane	118,000	59,200	27,500	138,000	69,400	33,700	165,000	86,000	45,400

TABLE 4. CONTROLLED EMISSION RATES OF TOTAL HYDROCARBONS AND VOC FOR VARIOUS INLET CONDITIONS AND OUTLET TEMPERATURES

Inlet stream description	Outlet temperature (°C)	Hydrocarbon emissions (mg/ℓ loaded)		Emission reduction[b] (mg/ℓ loaded)
		Total	VOC[a]	
High volatility				
15% organics	-62	61	59	360
	-73	30	28	390
	-84	14	12	410
30% organics	-62	59	56	780
	-73	29	26	820
	-84	14	11	830
50% organics	-62	52	48	1,460
	-73	27	21	1,480
	-84	14	8.7	1,500
Low volatility				
15% organics	-62	56	54	340
	-73	30	26	370
	-84	15	12	390
30% organics	-62	60	54	740
	-73	32	25	760
	-84	17	11	780
50% organics	-62	59	48	1,290
	-73	33	22	1,310
	-84	20	9.4	1,330

[a]Hydrocarbons excluding methane and ethane.

[b]This is approximately equal for VOC and total hydrocarbons.

Figures 6 through 9 illustrate the dependence of VOC emissions on condenser outlet temperature; while Figures 10 and 11 illustrate the dependence of VOC emissions on the total inlet organic concentration. As shown in Figures 8 and 9, the logarithm of the outlet non-methane/non-ethane hydrocarbon concentration is approximately proportional to the reciprocal of the condenser outlet temperature.

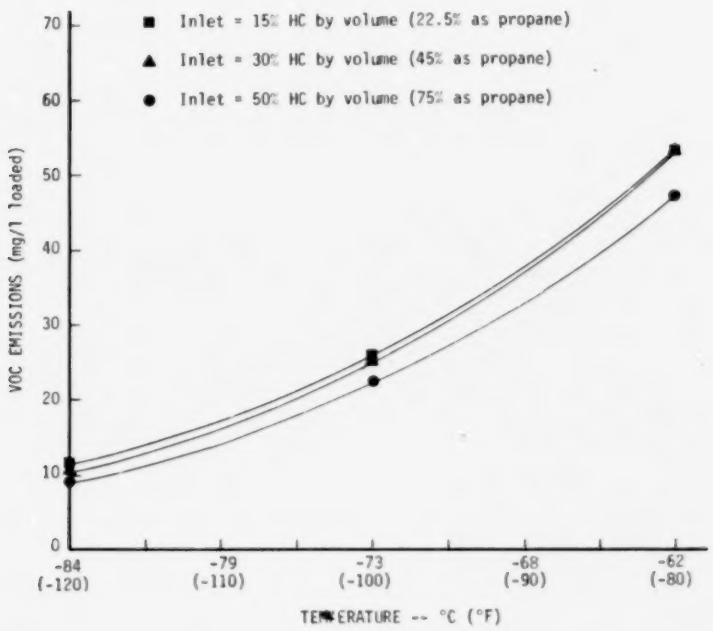

Figure 6. Effect of condenser outlet temperature on VOC emissions -- low volatility vapors.

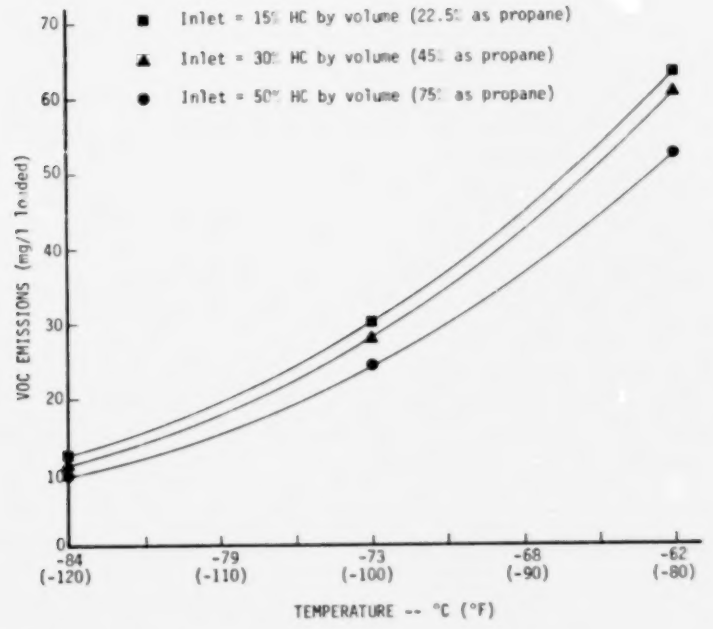

Figure 7. Effect of condenser outlet temperature on VOC emissions -- high volatility vapors.

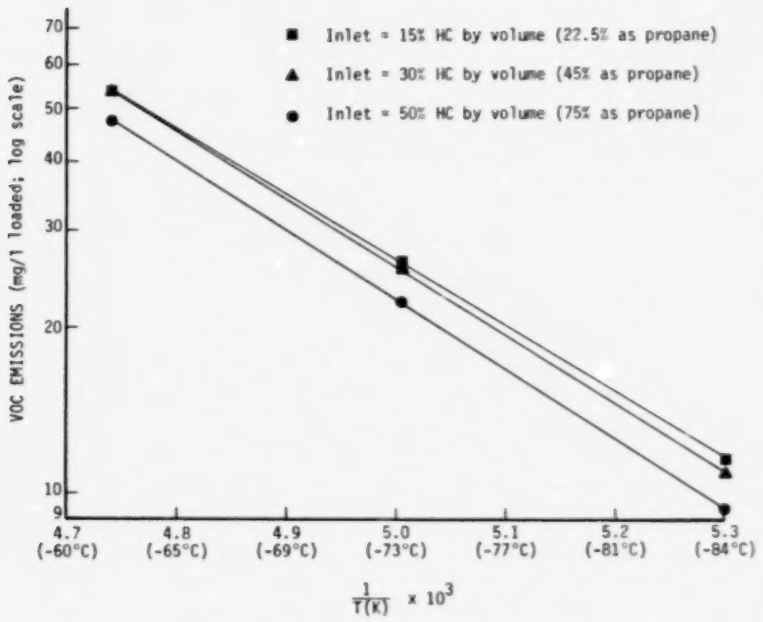

Figure 8. Effect of condenser outlet temperatures on VOC emissions -- low volatility vapors, log vs. 1/T scale.

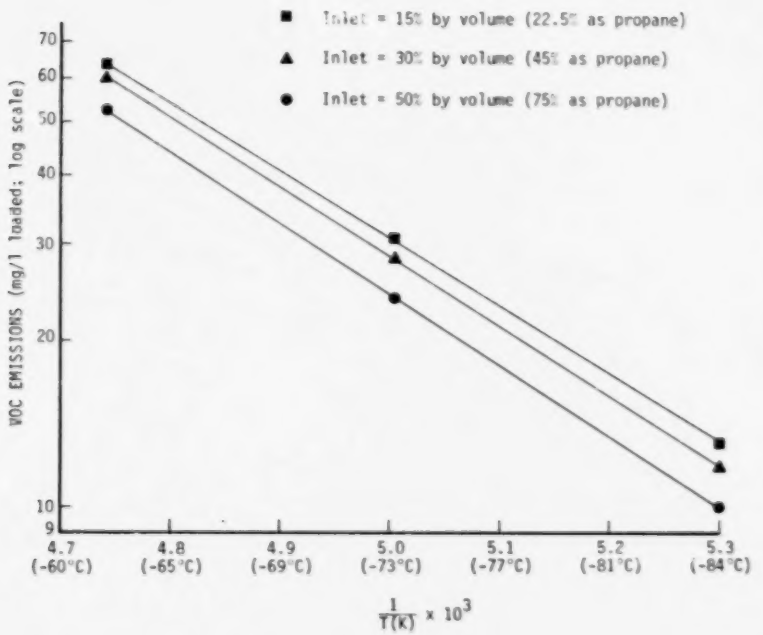

Figure 9. Effect of condenser outlet temperature on VOC emissions -- high volatility vapors, log vs. 1/T scale.

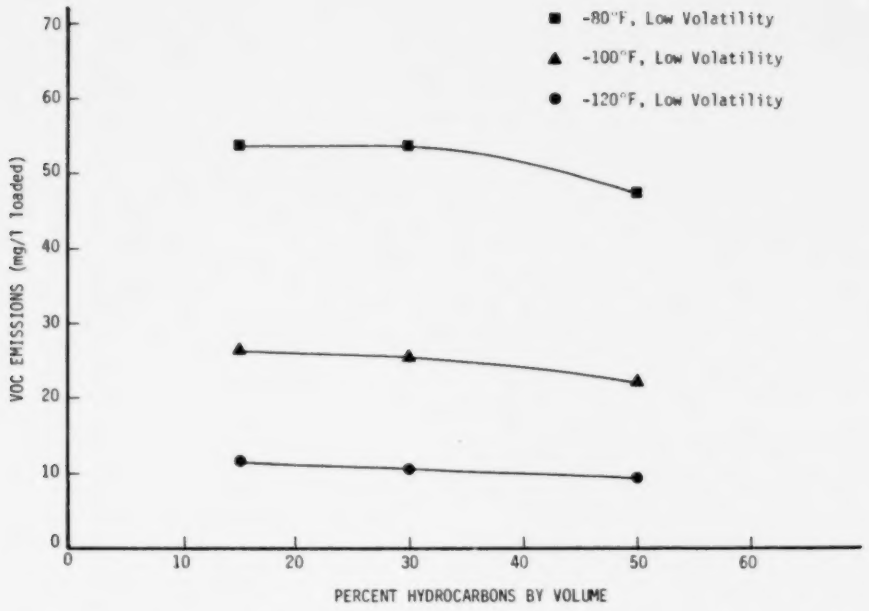

Figure 10. Effect of inlet organic content on VOC emissions -- low volatility vapors.

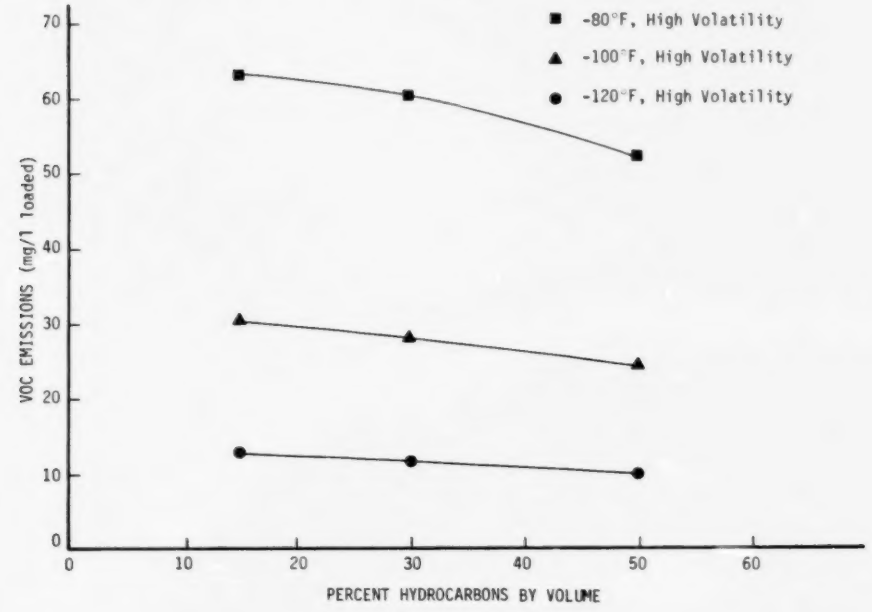

Figure 11. Effect of inlet organic content on VOC emissions -- high volatility vapors.

SECTION 4

ELECTRICAL ENERGY CONSUMPTIONS AND RELATIVE COSTS

GENERAL

The electrical energy requirement and cost of a refrigeration control system are dependent on the temperature or temperatures at which refrigeration is carried out, and the heat removal requirements for the system. The control systems considered in this study would first cool VOC/air mixtures to 4.4°C (40°F) in a precooler in order to remove most of the moisture present. Vapors from the precooler would then be cooled to -62°C, -73°C or -84°C in the main condenser. Thus, heat energy must be removed from the VOC/air mixture at 4.4°C and at -62°C, -73°C or -84°C.

Table 5 presents precooler and main condenser heat removal requirements for refrigeration systems cooling various inlet streams to the three outlet temperatures listed above. The inlet streams for which heat removal requirements are presented are high and low volatility gasoline vapors in concentrations of 15, 30, and 50 percent by volume in air.

The heat removal rates presented in Table 5 were calculated using total enthalpy values for the streams entering and leaving the precooler and leaving the main condenser. Enthalpy values were calculated in the same manner as equilibrium concentrations in the condenser outlet. The computer simulation program discussed in Section 2, and the SRK and PR methods of calculating thermodynamic property values discussed in Section 2 and Appendix A were used. The PR method was used to predict liquid density values, and the SRK method to predict other thermodynamic property values, including enthalpy values.

In order to calculate electrical energy requirements and relative system costs from the heat removal requirements presented in Table 5, a number of model systems were studied. Energy consumptions were estimated for systems controlling loading operations of four sizes, with the following average and maximum vapor flow rates:

Size	Average vapor flow (ℓ/day)	Maximum vapor flow (ℓ/min)
1	380,000	9,100
2*	950,000	14,000
3*	1,900,000	14,000
4	3,800,000	18,000

*Systems 2 and 3 have the same maximum vapor flow rate, but are operated on different schedules.

TABLE 5. HEAT REMOVAL REQUIREMENTS TO COOL VARIOUS INLET STREAMS TO VARIOUS TEMPERATURES

Input stream	Precooler heat removal requirement (J/ℓ loaded)	Cascade system heat removal requirements (J/ℓ loaded)		
		-62°C(-80°F) outlet	-73°C(-100°F) outlet	-84°C(-120°F) outlet
Summer[a]				
15 percent organics	36	260	300	320
30 percent organics	72	420	450	490
50 percent organics	200	520	560	590
Winter[b]				
15 percent organics	0	280	310	340
30 percent organics	0	480	520	550
50 percent organics	0	710	760	800

[a]Low volatility vapors; inlet temperature = 27°C (80°F).

[b]High volatility vapors; inlet temperature = 4.4°C (40°F).

For each of these loading operation sizes, systems designed to treat vapors containing 15, 30 and 50 percent hydrocarbons by volume and to operate at temperatures of -62°C, -73°C, and -84°C were studied. Thus, energy consumptions were estimated for a total of 36 model systems. In addition, for each model system energy usages were calculated for the control of vapor from high volatility and low volatility gasoline.

Three systems were studied in order to estimate the relative cost of refrigerating hydrocarbon-air mixtures to various temperatures. These model systems would refrigerate vapors from a typical loading operation to -62°C, -73°C, and -84°C. Each system would handle vapors containing 30 percent hydrocarbons from a loading operation of size number 3 above - that is: with an average vapor flow rate of 1,900,000 ℓ/day and a maximum flow rate of 14,000 ℓ/min. The ratios of the capital costs of these three systems were estimated to give an indication of the relative cost of cooling hydrocarbon-air mixtures to various cryogenic temperatures.

All of the model systems studied use the same refrigerants and have the same configuration. The differences between the systems are in refrigerant flow rates, and compressor and heat exchanger sizes. These differences arise from differences in operating temperature, cooling temperature, and cooling load. The basic configuration of the model systems used to estimate relative costs and energy consumptions was developed based on the design specifications of Edwards* Model DE refrigerated vapor condensers, because these models have been demonstrated to be capable of controlling hydrocarbon vapor emissions at existing gasoline loading facilities. The refrigerated vapor condenser configuration and design used in the model systems are described below.

MODEL REFRIGERATION SYSTEM DESIGN

Hydrocarbon vapors from gasoline loading are cooled from ambient temperature to -62°C, -73°C, or -84°C. The cooling takes place in two stages, the precooler and the main coil. Figure 12 is a schematic diagram of the system. Heat exchangers H-2 and H-3 in Figure 12 both represent sections of the main coil, while exchanger H-1 represents the precooler.

Incoming vapors, a mixture of hydrocarbons, water vapor, and air, are first cooled to 4.4°C in the precooler. The effect of this step is to condense a portion of the moisture content of the vapor, minimizing downstream icing problems. The precooler also reduces the system's energy consumption, by accepting part of the vapor's energy at a relatively high temperature.

The main heat exchanger coils (shown as H-2 and H-3, in Figure 12), cool the vapor from 4.4°C to -62°C, -73°C, or -84°C. This heat exchanger is cooled by freon R-503, which in turn is cooled by freon R-502 in a cascade refrigeration system. Chilled vapors from the main coil are released to the atmosphere. Condensed liquids from the precooler and the main coil drain to a product decanter, which removes water and recycles hydrocarbons to facility storage tanks.

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[a]Edwards Engineering Corp.
101 Alexander Ave., Pompton Plains, NJ 07444

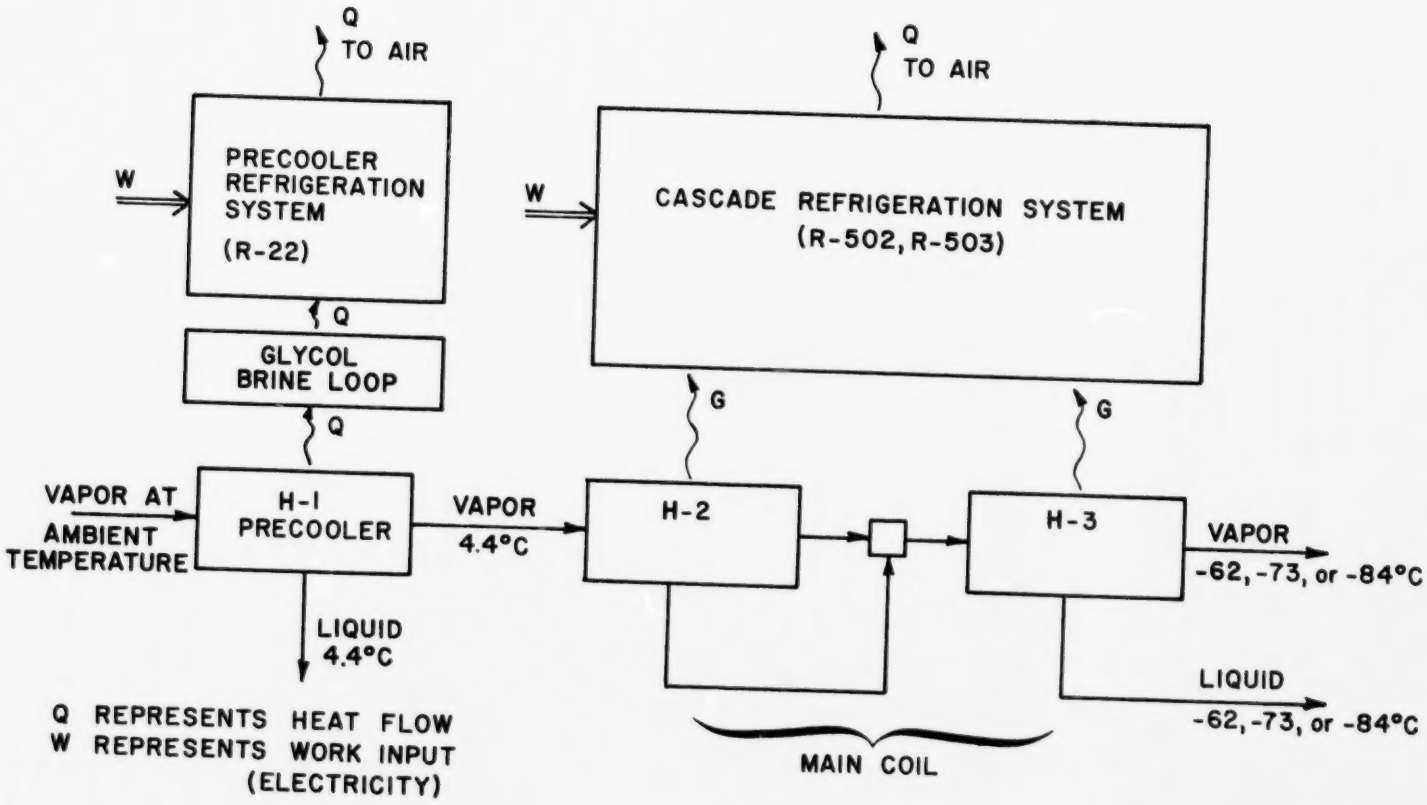

Figure 12. Vapor recovery system schematic.

Moisture that remains in the vapor stream as it enters the main coil condenses to form a hydrate on the surface of the first section of the coil (H-2). Defrosting is performed periodically by circulating warm trichloroethylene (TCE) through this section of the coil. The defrost cycle requires 75 minutes, after which the condenser must cool for approximately 45 minutes before reaching operating temperature. Ice must be removed periodically, usually once per day, so that the pressure drop through the coil does not become excessive. Thus, the vapor recovery unit is out of service for 2 hours out of every 24 hours.

Precooler Refrigeration System

The precooler refrigeration system is shown schematically in Figure 13. A vapor compressor refrigeration cycle, with freon R-22, is used to cool a glycol brine solution. The cold brine is stored in a reservoir until needed by the precoolers. This reservoir evens out the demand on the refrigeration system, by providing "stored refrigeration".

Refrigerant R-22 at state 1 in Figure 13 is a saturated liquid. It extracts heat from the glycol solution as it vaporizes. The saturated vapor then passes through a "liquid suction exchanger", or heat interchanger, where it accepts heat from the liquid R-22 stream. The effect of this interchanger is to superheat the vapor and subcool the liquid. It usually improves the energy efficiency of a system, and in this case reduces compressor energy consumption by 24 percent. The R-22 vapor is then compressed and condensed in an air-cooled heat exchanger. It then passes through the other side of the interchanger and through an expansion valve, returning to state 1, a saturated liquid.

Cascade Refrigeration System

The cascade refrigeration system, shown in Figure 14, is made up of two vapor compression refrigeration cycles, each similar to the precooler cycle. The high stage uses R-502 for heat transfer. It operates between a condenser temperature of $60^{\circ}C$ ($140^{\circ}F$) and an evaporator temperature of $-32^{\circ}C$ ($-25^{\circ}F$). The high stage evaporator is also the low stage condensor, forming the cascade system.

The low stage, using R-503, cycles between $-29^{\circ}C$ ($-20^{\circ}F$) in the condenser and $-65^{\circ}C$, $-76^{\circ}C$, or $-87^{\circ}C$ ($-85^{\circ}F$, $-105^{\circ}F$, or $-125^{\circ}F$) in the evaporator. The low stage evaporator is the main coil of the vapor recovery unit, and chills the hydrocarbon vapors to $-62^{\circ}C$, $-73^{\circ}C$, or $-84^{\circ}C$.

Each of the cascade cycles is slightly different from the precooler cycle, in that they contain desuperheaters. The high stage contains a glycol heater (which warms the defrost brine) immediately following the compressor. This position in the low stage is filled by an air cooled coil, ventilated by the same fan as the high stage condenser. The high stage interchanger reduces compressor power consumption in that stage by 34 percent; the low stage interchanger has no effect on the low stage compressor, but slightly reduces the amount of power needed by the high stage compressor.

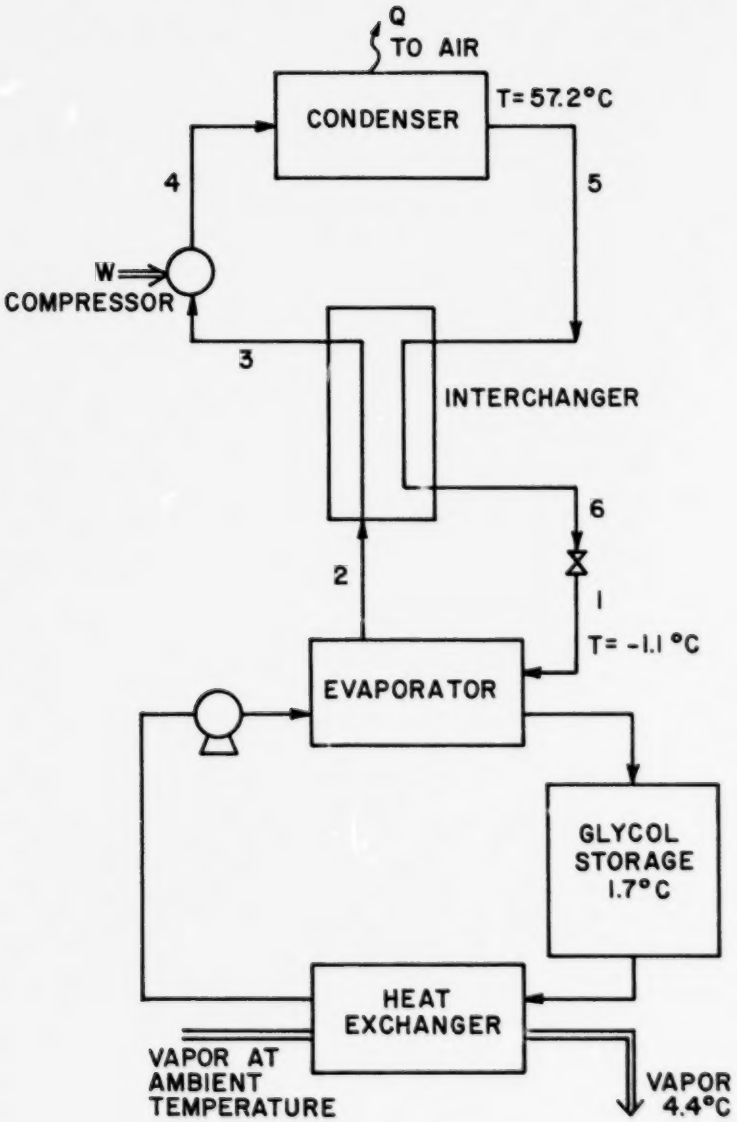

Figure 13. Precooler refrigeration cycle (R-22).

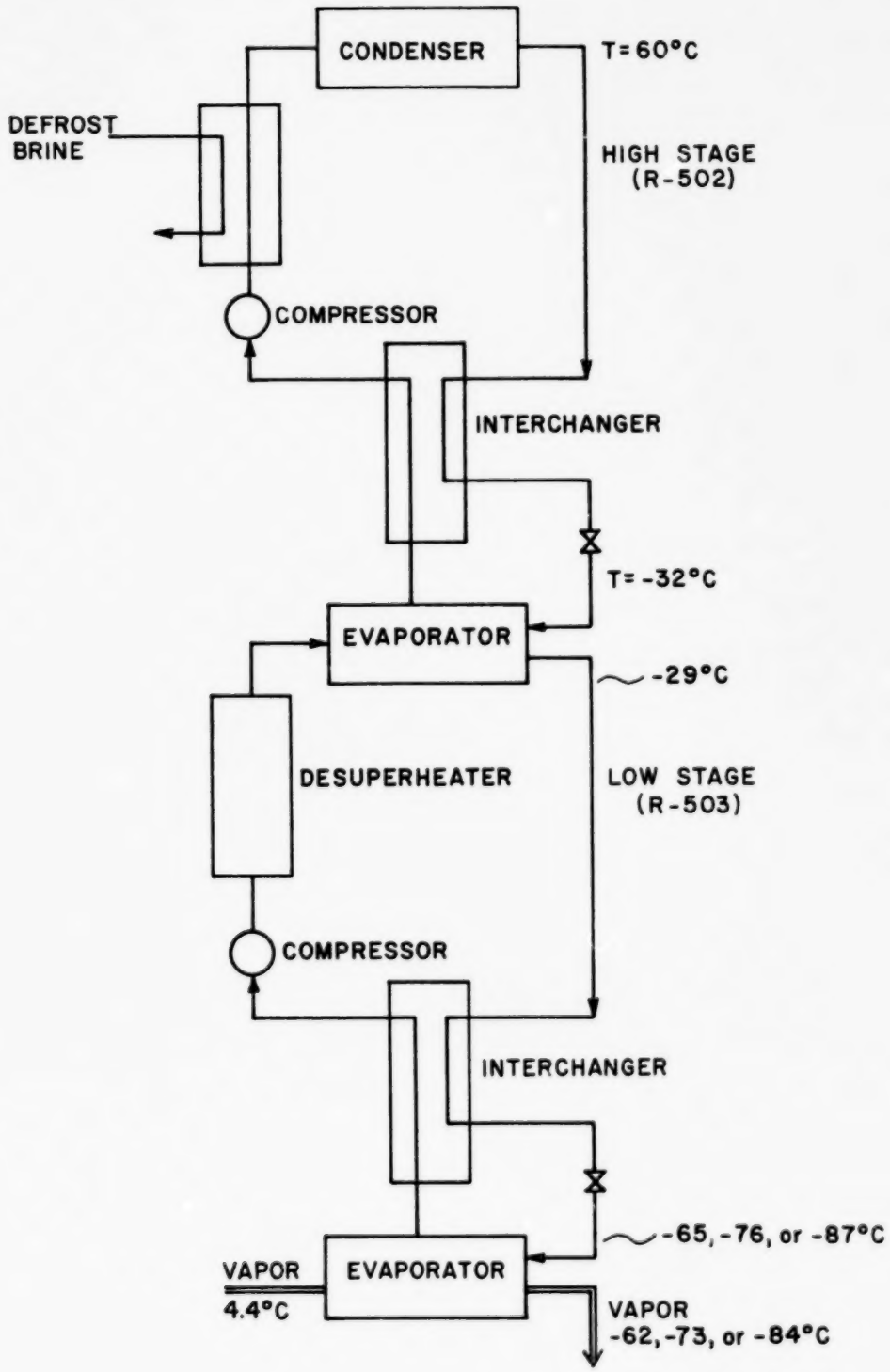

Figure 14. Cascade refrigeration system.

ENERGY REQUIREMENTS

Using published refrigerant property data, the compressor energy requirement to remove a given amount of heat can be calculated for a refrigeration system of the design described above.[7] The compressor energy requirement is the major energy requirement for the model system configuration described in the previous section. Precooler brine pump requirements and fan requirements are minor in comparison with compressor requirements.

The electricity use of the precooler compressor per unit of heat removed from the precooler, and the electricity requirements of the low stage and high stage compressors per unit of heat removed in the main condenser are presented in Table 6. These electricity requirements were calculated assuming a cycle efficiency of 75 percent of the work input and using 2.8°C (5°F) temperature differences across all heat exchangers. Refrigerant enthalpies, temperatures, and pressures at each stage of the precooler and low stage and high stage refrigeration cycles are presented in Appendix B. The low stage refrigerant states differ depending on the temperature of the main condenser. For the precooler and the high stage cooler, the refrigerant states do not depend on the main condenser temperature; however, the flow rate of refrigerant through the high stage cycle, and hence the electricity requirement of the high stage compressor increase as the temperature of the main condenser decreases.

From the heat removal requirements presented in Table 5 and the ratios of compressor electricity use to heat removal presented in Table 6, the electricity required to cool the various inlet streams under study to the three system outlet temperatures can be estimated. Electricity requirements to cool high and low volatility vapors in concentrations of 15, 30, and 50 percent by volume to -62°C, -73°C and -84°C are presented in Table 7.

In addition to the heat which must be removed by a refrigeration system from the VOC/air mixture fed to it, additional energy must be removed as a result of heat leaks into the system from the outside environment. The heat leak rate for a system does not depend on the vapor flow rate through the system, but instead depends on the design maximum capacity of the system. Hence, the electricity requirement per volume of inlet vapor varies with the ratio of maximum system capacity to average system throughput. Heat leak rates were estimated as a function of system size using heat exchanger operating temperatures and estimated exposed surface areas. The heat leak rates were calculated assuming a heat flow rate of about 0.14 J/sec-m^2-°C, which corresponds to about 15 cm (6 in) of polyurethane insulation on all exposed cold surfaces.[7] Compressor electricity requirements due to heat leaks were calculated for refrigeration systems operating at -62°C, -73°C and -84°C, and designed to control VOC/air mixtures with 15, 30, and 50 percent VOC by volume from loading operations of the following four sizes.

TABLE 6. COMPRESSOR ELECTRICITY REQUIREMENTS OF MODEL REFRIGERATION SYSTEMS PER UNIT HEAT REMOVAL REQUIREMENT

Refrigeration system	Compressor electricity requirement per heat removed (Wsec/J)
Precooler[a]	0.33
Cascade systems	
-62°C (-80°F) outlet	1.25
-73°C (-100°F) outlet	1.44
-84°C (-120°F) outlet	1.74

[a]Precooler electricity requirements do not depend on the cascade system outlet temperature.

TABLE 7. COMPRESSOR ELECTRICITY REQUIREMENTS TO COOL VARIOUS INLET STREAMS TO VARIOUS TEMPERATURES WITH NO HEAT LEAKS

Input stream	Compressor electricity requirements with no heat loss (Whr/ℓ loaded)[a]		
	-62°C (-80°F) outlet	-73°C (-100°F) outlet	-84°C (-120°F) outlet
Summer[b]			
15 percent organics	0.10	0.13	0.17
30 percent organics	0.17	0.21	0.26
50 percent organics	0.22	0.27	0.33
Winter[c]			
15 percent organics	0.11	0.14	0.19
30 percent organics	0.17	0.21	0.27
50 percent organics	0.23	0.29	0.37

[a]Compressors were assumed to be 90 percent efficient.

[b]Low volatility vapors; inlet temperature = 27°C (80°F).

[c]High volatility vapors; inlet temperature = 4.4°C (40°F).

Size	Average vapor flow (ℓ/day)	Maximum vapor flow (ℓ/min)
1	380,000	9,100
2	950,000	14,000
3	1,900,000	14,000
4	3,800,000	18,000

Thus, electricity consumptions due to heat leaks were estimated for a total of 36 model systems. These estimates are presented in Table 8.

As can be seen from a comparison of Tables 6 and 7, the electricity requirement due to heat leaks ranges from about 26 percent for model systems of size 1 to 4.0 percent for model systems of size 4. Total annual average electricity requirements for the 36 model systems described above are presented in Table 9. It was assumed that the systems would treat low volatility vapors for six months of the year and high volatility vapors for the remaining six months.

RELATIVE COSTS

Capital Costs

Relative capital costs have been estimated for refrigeration systems designed to cool VOC/air mixtures containing 30 percent VOC by volume to -62°C, -73°C, and -84°C at a maximum inlet flow rate of 14,000 ℓ/min. This maximum flow rate corresponds to system size 3. The relative capital costs were estimated by estimating the costs of the major components of each of the three systems. Cost estimates were taken from published sources, and all costs were updated to 1980 dollars using cost indices published in Chemical Engineering.[8-11] Components included in the cost estimates were compressors, condensers, heat exchangers, pumps, fans, and sheet metal for storage tanks, duct work, and encasing the total system. It should be noted that the total costs are representative of the cost to manufacture refrigeration systems. Refrigeration control systems for bulk gasoline terminals are not generally built by the terminal owner, but are purchased as package units from a manufacturer. Therefore the costs derived for the model systems do not include manufacturer's and vendor's profits or savings which might be achievable by mass production. Also, the cost estimates do not include costs for plumbing, wiring, refrigerant and brine costs, inventory of spare parts, installation costs (i.e., installation of components into the system as well as installation of the system at the operating site), freight and handling, and duties and taxes. Thus, the capital cost estimates do not necessarily reflect the real costs of refrigeration systems but can be used to adequately determine ratios of capital costs for the three systems discussed. The cost of the -84°C system is approximately 9 percent higher than the cost of the -73°C system, which is approximately 12 percent higher than the cost of the -62°C system. The relationships between system capital costs and VOC emissions are illustrated in Figure 15. The data presented in these figures were derived using the above ratios and emission rates presented in Table 4.

TABLE 8. COMPRESSOR ELECTRICITY REQUIREMENTS RESULTING FROM HEAT LEAKS FOR VARIOUS SYSTEM FLOW RATES, INLET CONCENTRATIONS, AND OUTLET TEMPERATURES

	Compressor electricity requirements due to heat loss for various system design and maximum flow rate (Whr/ℓ loaded)			
	Size 1[a]	Size 2[b]	Size 3[c]	Size 4[d]
15 percent organics				
-62°C (-80°F) outlet	0.029	0.015	0.0076	0.0045
-73°C (-100°F) outlet	0.036	0.020	0.0097	0.0057
-84°C (-120°F) outlet	0.049	0.027	0.013	0.0078
30 percent organics				
-62°C (-80°F) outlet	0.044	0.024	0.012	0.0070
-73°C (-100°F) outlet	0.055	0.029	0.014	0.0086
-84°C (-120°F) outlet	0.070	0.038	0.019	0.011
50 percent organics				
-62°C (-80°F) outlet	0.060	0.032	0.016	0.0094
-73°C (-100°F) outlet	0.075	0.041	0.020	0.012
-84°C (-120°F) outlet	0.096	0.052	0.026	0.015

[a]Size 1: average flow = 380,000 ℓ/day; maximum flow = 9,100 ℓ/min.
[b]Size 2: average flow = 950,000 ℓ/day; maximum flow = 14,000 ℓ/min.
[c]Size 3: average flow = 1,900,000 ℓ/day; maximum flow = 14,000 ℓ/min.
[d]Size 4: average flow = 3,800,000 ℓ/day; maximum flow = 18,000 ℓ/min.

TABLE 9. TOTAL COMPRESSOR ELECTRICITY REQUIREMENTS FOR VARIOUS SYSTEM FLOW RATES, INLET CONCENTRATIONS AND OUTLET TEMPERATURES

	Total average compressor electricity requirements (Whr/ℓ loaded)			
	Size 1[a]	Size 2[b]	Size 3[c]	Size 4[d]
15 percent organics				
-62°C (-80°F) outlet	0.13	0.12	0.11	0.11
-73°C (-100°F) outlet	0.17	0.16	0.15	0.14
-84°C (-120°F) outlet	0.23	0.21	0.19	0.19
30 percent organics				
-62°C (-80°F) outlet	0.21	0.19	0.18	0.18
-73°C (-100°F) outlet	0.27	0.24	0.22	0.22
-84°C (-120°F) outlet	0.34	0.30	0.28	0.28
50 percent organics				
-62°C (-80°F) outlet	0.29	0.26	0.24	0.23
-73°C (-100°F) outlet	0.36	0.32	0.30	0.29
-84°C (-120°F) outlet	0.45	0.40	0.38	0.36

[a]Size 1: average flow = 380,000 ℓ/day; maximum flow = 9,100 ℓ/min.
[b]Size 2: average flow = 950,000 ℓ/day; maximum flow = 14,000 ℓ/min.
[c]Size 3: average flow = 1,900,000 ℓ/day; maximum flow = 14,000 ℓ/min.
[d]Size 4: average flow = 3,800,000 ℓ/day; maximum flow = 18,000 ℓ/min.

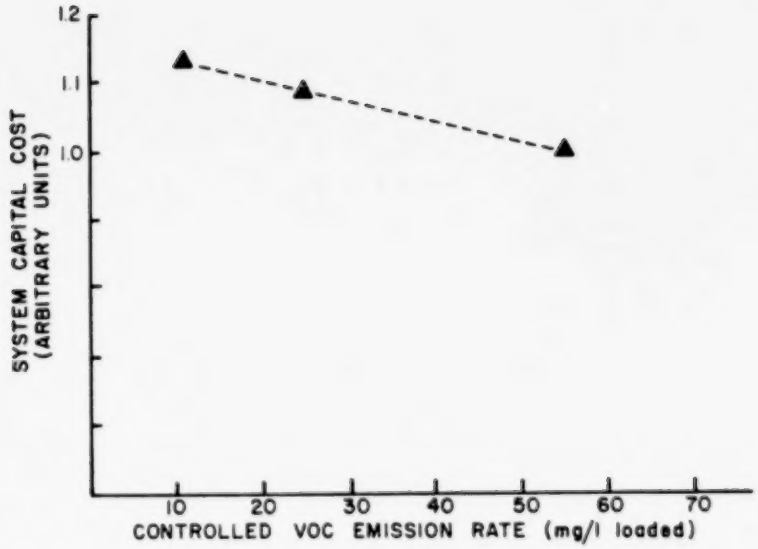

Figure 15. Variation of system capital cost with controlled VOC emission rate for systems designed to cool VOC/air mixtures containing 30 percent VOC by volume to temperatures of -62°C, -73°C, and -84°C at a maximum flow rate of 14,000 ℓ/min.

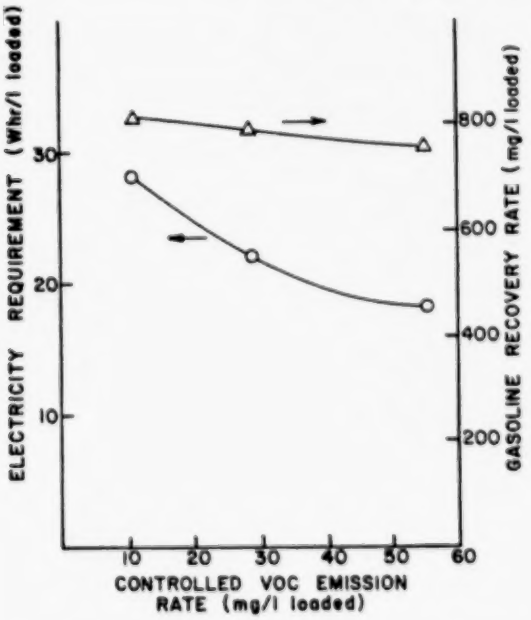

Figure 16. Variation of system electricity requirement and gasoline recovery rate with controlled VOC emission rate for systems designed to cool VOC/air mixtures containing 30 percent VOC by volume to temperatures of -62°C, -73°C, and -84°C at a maximum flow rate of 14,000 ℓ/min.

Electricity Costs and Gasoline Recovery Credits

Any consideration of energy costs for refrigeration control systems should also include the value of gasoline recovered. Electricity requirements for various model systems have been presented in Table 9. Gasoline vapor recovery rates are approximately equal to the emission reduction rates presented in Table 4.

Table 10 compares the cost of electricity to the value of recovered gasoline for three systems designed to cool VOC/air mixtures containing 30 percent by volume VOC at a maximum flow rate of 14,000 ℓ/min (system size 3) to -62°C, -73°C and -84°C. The values presented are averages, with the assumption that high and low volatility gasolines are loaded in equal amounts in the long term. An electricity cost of $0.06/kWhr and a recovered gasoline value of $0.236/kg gasoline were used.

The data presented in Table 10 indicate that the value of recovered gasoline exceeds the cost of electricity for all three outlet conditions. However, the increase in gasoline recovered is much less than the increase in electricity requirement as system temperature is decreased. Figure 16 illustrates the variation of gasoline recovery rate and electricity use with VOC emission rate.

TABLE 10. COMPARISON OF ELECTRICITY COST AND RECOVERED GASOLINE VALUE FOR REFRIGERATION TO VARIOUS TEMPERATURES[a]

Outlet temperature	Electricity cost ($/Mℓ loaded)	Recovered gasoline value ($/Mℓ loaded)
-62°C (-80°F)	11	179
-73°C (-100°F)	13	186
-84°C (-120°F)	17	189

[a]Inlet gasoline vapor concentration = 30 percent by volume. System size 3: average vapor flow = 1,900,000 ℓ/day; maximum flow = 14,000 ℓ/min. Values presented are averages for high volatility vapors fed at 4.4°C and low volatility vapors fed at 27°C.

REFERENCES

1. Standards of Performance for New Stationary Sources; Emissions Limitation of Volatile Organic Compounds From Gasoline Tank Truck Loading Racks at Bulk Gasoline Terminals. Federal Register, 45(244): 83126-83153. December 17, 1980

2. Bulk Gasoli..e Terminals--Background Information for Proposed Standards. EPA-450/3-80-038a, U.S. Environmental Protection Agency, Research Triangle Park, NC. 1980.

3. Recommended Policy on Control of Volatile Organic Compounds. Federal Register, 42(131): 35314-35316.

4. Gasoline Vapor Recovery Efficiency Testing Performed at the Phillips Fuel Company Bulk Loading Terminal, Hackensack, NJ. EMB Test Report No. 77-GAS-19, U.S. Environmental Protection Agency, Research Triangle Park, NC. 1977.

5. Benzene Control Efficiency of Vapor Processor at the Exxon Bulk Gasoline Loading Terminal, Philadelphia, PA. EMB Test Report No. 78-BEZ-4, U.S. Environmental Protection Agency, Research Triangle Park, NC. 1978.

6. West, E.H. and J.H. Erbar. An Evaluation of Four Methods of Predicting the Thermodynamic Properties of Light Hydrocarbon Systems. Paper presented at the 52nd Annual Meeting, NGPA, Dallas, Texas, March 26-28, 1973.

7. ASHRAE Handbook and Product Directory, 1977 Fundamentals. American Society of Heating, Refrigeration, and Air Conditioning Engineers, Inc. 1977.

8. Dryden, Charles E. and Richard H. Furlow, Chemical Engineering Costs, The Ohio State University, Columbus, Ohio, 1966.

9. GPSA, Engineering Data Book, Ninth Edition. Gas Processors Association. 1972.

10. Perry, Robert H. and Cecil H. Chilton, Chemical Engineer's Handbook, Fifth Edition, McGraw-Hill Book Company, 1973.

11. Peters, Max S. and Klaus D. Timmerhaus, Plant Design and Economics for Chemical Engineers, McGraw-Hill Book Company, New York, 1968.

APPENDIX A

METHODS OF GENERATING EQUILIBRIUM DATA

Vapor/liquid phase equilibrium relationships for hydrocarbon mixtures are generally determined in terms of the equilibrium vaporization ratio, or K factor:

$$K_i = \frac{Y_i}{X_i} \tag{1}$$

where K_i = the equilibrium vaporization ratio for component i

Y_i = the mole fraction of component i in the vapor phase

X_i = the mole fraction of component i in the liquid phase

K factors for various components are generally predicted using the following basic formula:

$$K_i = \frac{\gamma_i^L \phi_i^L}{\gamma_i^V \phi_i^V} \tag{2}$$

where γ_i^L = the activity coefficient of component i in the liquid phase

γ_i^V = the activity coefficient of component i in the vapor phase

φ_i^L = the fugacity coefficient of component i in the liquid phase

ϕ_i^V = the fugacity coefficient of component i in the vapor phase

A number of methods have been devised to calculate fugacities and activities of component mixtures, and thus estimate K values at various temperatures and pressures. Generally, the activity coefficients are assumed to be equal to 1, and an equation of state is used to calculate K_i from the pressure-volume-temperature relationship of a fluid as defined in the equation of state. Several commonly used methods of developing K factors, and their advantages and drawbacks, are described briefly below.

The Soave-Redlich-Kwong and Peng-Robinson methods appear to give the best results in the cryogenic region. They require the smallest number of pure component parameters as input and appear to have the widest temperature-pressure range of any of the correlations discussed. Both of these methods are accurate for pressures up to about 35,000 kPa (5,000 psia) and over the temperature range from -155°C (-250°F) to 260°C (500°F).

Benedict-Webb-Rubin (BWR) Equation of State

The Benedict-Webb-Rubin equation is the most widely-used procedure for calculating the properties of a large number of gases over a wide range of conditions.[2] The equation, in its original form, uses eight parameters for each component in a mixture plus a tabular temperature dependence for one of the parameters to improve the fit of vapor pressure data.[3]

The original equation is

$$P = RTd + (B_oRT - A_o - C_o/T^2)d^2 + (bRT - a)d^3 + a\alpha\, d^6 + \frac{cd^3}{T^2}(1 + \beta d^2)\exp(-\beta d^2) \qquad (3)$$

or

$$Z - 1 = \left(B_o - \frac{A_o}{RT} - \frac{C_o}{RT^3}\right)d + \left(b - \frac{a}{RT}\right)d^2 + \frac{a\alpha}{RT}\,d^5 + \frac{cd^2}{RT^3}(1 + \beta d^2)\exp(-\beta d^2) \qquad (4)$$

where B_o, C_o, A_o, b, a, c, β, α = Coefficients for BWR equation

d = Density, g-mole/ℓ

P = Pressure, kPa

R = Gas constant = 1.98 cal/mole K

T = Temperature, Kelvin

V = Specific volume, ℓ/g-mole

Z = Compressibility factor, $\frac{PV}{RT}$

This equation is reasonably accurate for light paraffin mixtures at reduced temperatures of 0.6 and above. (Reduced temperature, T_r is defined as T/T_c, where T_c is the critical temperature of the compound under study.) However, it has difficulty with low temperatures, nonhydrocarbons, nonparaffins, and heavy paraffins. Modified BWR equations have recently been developed that are capable of predicting light paraffin K-values at cryogenic temperatures.[2,4,5]

The Redlich-Kwong Equation of State

The Redlich-Kwong equation was formulated in 1949 and is considered the most successful two-parameter equation of state.[6] Although volumetric and thermal properties of pure components can be predicted with a good deal of accuracy, its prediction of multicomponent vapor-liquid equilibria often gives poor results.[7]

The Redlich-Kwong equation is, as originally proposed,[8]

$$P = \frac{RT}{V - b} - \frac{a}{T^{0.5}V(V + b)} \tag{5}$$

or

$$Z = \frac{V}{V - b} - \frac{a}{RT^{1.5}(V + b)}$$

where a, b = Parameters in Redlich-Kwong equation

The Chao-Seader Correlation

The Chao-Seader correlation uses the Redlich-Kwong equation to calculate the vapor phase fugacity coefficient; the Hildebrand equation, based on regular solution theory for liquid-mixture nonideality, to calculate liquid phase activity coefficients; and a pure-liquid property correlation to calculate the pure liquid component fugacity coefficient at system conditions.[1,9,10,11] The Chao-Seader correlation as a function of these three factors is

$$K_i = \frac{\gamma_i^L \ \phi_i^L}{\phi_i^V} \tag{6}$$

where γ_i^V is assumed to be equal to 1.0.

The liquid phase activity coefficients are evaluated using the Hildebrand equation

$$\ln \gamma_i^L = \frac{V_i \ (\delta_i - \overline{\delta})^2}{RT} \tag{7}$$

where

$$\overline{\delta} = \frac{\Sigma_i X_i \ V_i \ \delta_i}{\Sigma_i \ X_i \ V_i}$$

and δ_i = Solubility parameter for component i

$\overline{\delta}$ = Average solubility parameter for the mixture

The vapor fugacity coefficient is calculated as follows:

$$\ln \phi_i^V = (Z - 1) \frac{B_i}{B} - \ln (Z - BP) - \frac{A^2}{B} \left[2 \frac{A_i}{A} - \frac{B_i}{B}\right] \ln \left(1 + \frac{BP}{Z}\right) \tag{8}$$

where A_i, B_i = Constants for component i which are functions of the component's critical temperature and pressure.

A, B = mole fraction weighted averages of A_i and B_i

Z is obtained by solution of Redlich-Kwong equation.

The pure liquid fugacity coefficients are evaluated within the framework of Pitzer's modified form of the principle of corresponding states:

$$\text{Log } \phi_i^L = \text{Log } \phi_i^{(o)} + \omega_i \text{ Log } \phi_i^{(1)} \qquad (9)$$

where ω_i = Acentric factor for component i

$\phi_i^{(o)}$ = Fugacity coefficient for a simple fluid

$\phi_i^{(1)}$ = A correction term for departure from simple fluids.

The Chao-Seader method will predict reasonably accurate K values for mixtures of light hydrocarbons at the conditions listed below.[11]

- Temperature: -20 to 250°C (0 to 500°F)
- Pressure: < 10,000 kPa (1500 psia)
- For hydrocarbons except methane $0.5 \leq T_r \leq 1.3$
- The concentration of hydrogen and methane in the liquid phase should not exceed 20 percent of other dissolved gases.

The Soave-Redlich-Kwong Equation of State

The Soave-Redlich-Kwong (SRK) equation is a modification of the Redlich-Kwong equation published in 1972 by Georgio Soave.[7] Soave replaced the term $a/T^{0.5}$ with a more general temperature dependent term:[11]

$$P = \frac{RT}{V - b} - \frac{(a_c\ \alpha)}{V\ (V + b)} \quad \text{or} \quad Z^3 - Z^2 + Z\ (A - B - B^2) - AB = 0 \qquad (8)$$

where $(a_c\ \alpha) = \Sigma_i\ \Sigma_j\ X_i\ X_j\ a_{ci}^{.5}\ a_{cj}^{.5}\ \alpha_i^{.5}\ \alpha_j^{.5}\ (1 - K_{ij}^*)$

$a_{ci} = 0.42747\ R^2\ T_{ci}^2/P_{ci}$

$\alpha_i^{.5} = 1 + m_i\ (1 - T_{ri}^{.5})$

$m_i = 0.480 + 1.574\omega_i - 0.176\omega_i^2$

$b = 0.08664\ RT_{ci}/P_{ci}$

$A = (a_c\ \alpha)\ P/\ (R^2\ T^2)$

$B = bP/T$

K_{ij}^* = empirical correction factor determined by the behavior of a binary mixture of components i and j.

T_{ci} = critical temperature of component i, K

P_{ci} = critical pressure of component i, kPa

T_{ri} = reduced temperature for component i, T/T_{ci}

P_{ri} = reduced pressure for component i, P/P_{ci}

Similarity of Equation (10) to the Van der Waals equation is apparent. K values are predicted by the SRK method with the relationship:

$$K_i = \frac{\phi_i^L}{\phi_i^V} \tag{11}$$

The SRK equation has one limitation which must be noted. While the liquid compressibility factor is of sufficient accuracy for prediction of liquid fugacity coefficients, it has been found to be somewhat inaccurate for liquid density prediction, often yielding values 10 to 20 percent low.[11]

The SRK method is being widely used for a variety of mixtures of hydrocarbons with reasonable results for cryogenic systems (to -155°C or -250°F) up to 33,000 kPa.[11] The SRK equation is reported to be very accurate when used to predict vapor-liquid equilibria and enthalpy departures for light hydrocarbon systems.[12]

The Peng-Robinson Equation of State

The Peng-Robinson equation is similar to the SRK equation and was meant to address the two weaknesses of the SRK equation:[11,13]

- Instability at critical point, and
- Inaccurate liquid density prediction.

The Peng-Robinson equation is

$$P = \frac{RT}{V - b} - \frac{a}{V(V + b) + b(V - b)} \tag{12}$$

or

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \tag{13}$$

where $A = aP/R^2T^2$

$B = bP/RT$

$a = \Sigma_i \Sigma_j X_i X_j a_{ij}$

$b = \Sigma_i X_i b_i$

$$a_i = (0.45724\ R^2T_{ci}^2/P_{ci})$$

$$b_i = 0.0778\ RT_{ci}/P_{ci}$$

$$a_{ij} = (1 - K^*_{ij})\ a_i^{.5}\ a_j^{.5}$$

$$\alpha^{.5} = 1 + M_i\ (1-T_r^{.5})$$

$$M_i = 0.37464 + 1.54226\ \omega_i - 0.26992\ \omega_i^2$$

The Peng-Robinson equation may be used interchangeably with the SRK equation. For most mixtures and conditions, results will be nearly identical to those produced by SRK.[11]

KEY OF TERMS USED IN APPENDIX A

superscripts L and V refer, respectively, to the liquid and vapor phases

subscripts i and j are used to refer to particular mixture components

subscript c is used to indicate that the variable is a function of a critical property such as critical temperature, T_c, or critical pressure, P_c, which are defined below

all subscripted forms of a, A, α, b, B, β, c, C are parameters used in the various equations and are defined as they are used

d = density, g-mole/liter

K_i = equilibrium vaporization ratio for component i

K^*_{ij} = empirical correction factor used in the SRK and PR equations which is determined by the behavior of a binary mixture of components i and j.

M_i, m_i = functions of the acentric factor, ω_i

P = pressure, kPa

P_{ci} = critical pressure of component i

P_{ri} = reduced pressure of component i, P/P_{ci}

R = gas constant, 1.98 cal/mole K

T = temperature, K

T_{ci} = critical temperature of component i

T_{ri} = reduced temperature of component i, T/T_{ci}

V = specific volume, ℓ/g-mole

X_i = mole fraction of component i in the liquid phase

Y_i = mole fraction of component i in the vapor phase

Z = compressibility factor, $\frac{PV}{RT}$

γ_i^L = activity coefficient of component i in the liquid phase

γ_i^v = activity coefficient of component i in the vapor phase

δ_i = solubility parameter for component i

$\overline{\delta}$ = average solubility parameter for the mixture

ϕ_i^L = fugacity coefficient of component i in the liquid phase

ϕ_i^V = fugacity coefficient of component i in the vapor phase

$\phi_i^{(o)}$ = fugacity coefficient of a simple fluid

$\phi_i^{(o)}$ = a correction factor for departure of fugacity from that of a simple fluid

ω = acentric factor for component i

REFERENCES FOR APPENDIX A

1. GPSA, Engineering Data Book, Ninth Edition. Gas Processors Association. 1972.

2. Hansen, R.E. Low-Temperature BWR Equation. Gas Processors Association. Proceedings of 48th Annual Convention. 1969. p. 52.

3. Benedict, M., G.B. Webb, and L.C. Rubin. An Empirical Equation for Thermodynamic Properites of Light Hydrocarbons and their Mixtures. Chemical Engineering Progress. Volume 47, No. 8, 1951. p. 419.

4. Starling, K.E., J.E. Powers. IEC Fund., Volume 9, No. 4, 1970. p. 531.

5. Starling, K.E. Fluid Thermodynamic Properties for Light Petroleum Systems. Gulf Publishing Co., 1973. p. 270.

6. Reid, R.C., J.M. Prausnitz, and T.K. Sherwood. The Properites of Gases and Liquids, Third Edition. McGraw-Hill Book Co., 1977. p. 688.

7. Soave, G. Equilibrium Constants from a Modified Redlich-Kwong Equation of State. Volume 27, No. 6, 1972. p. 1197.

8. Redlich, O., and J.N.S. Kwong. On the Thermodynamics of Solutions - An Equation of State. Chem Rev., Volume 44, 1949. p. 233.

9. Chao, K.D., and J.D. Seader. A General Correlation of Vapor-Liquid Equilibria in Hydrocarbon Mixtures. A.I.Ch.E. Journal, Volume 7, December 1961. pp. 598-605.

10. Hildebrand, H.H., and R.L. Scott. The Solubility of Nonelectrolytes, 3rd Edition. Reinhold, New York, 1959.

11. Simulation Sciences Inc. Process Simulation Program Reference Manual. 1980.

12. West, E.H., and J.H. Erbar. An Evaluation of Four Methods of Predicting the Thermodynamic Properties of Light Hydrocarbon Systems. Paper presented at 52nd Annual Meeting, NGPA, Dallas, Texas, March 26-28, 1973.

13. Peng, D.Y., and D.B. Robinson. A New Two-Constant Equation of State. Ind. Eng. Chem. Fundam., Vol. 15, No. 1, 1976. p. 59.

APPENDIX B

THERMODYNAMIC DESCRIPTIONS OF REFRIGERANT CYCLES

KEY

H_i = enthalpy of the refrigerant in state i

P_i = pressure of the refrigerant in state i

T_i = temperature of the refrigerant in state i

Q = refers to heat flow

W = refers to work input (W can be expressed in terms of Q, since both refer to rates of energy flow)

A total cycle efficiency of 75 percent of the work input was used. Inefficiencies in the system include compressor inefficiency and inefficiency due to non-adiabatic conditions in the expander.

The source of refrigerant properties data was:

ASHRAE Handbook and Product Directory, 1977 Fundamentals. American Society of Heating, Refrigeration, and Air Conditioning Engineers, Inc. 1977.

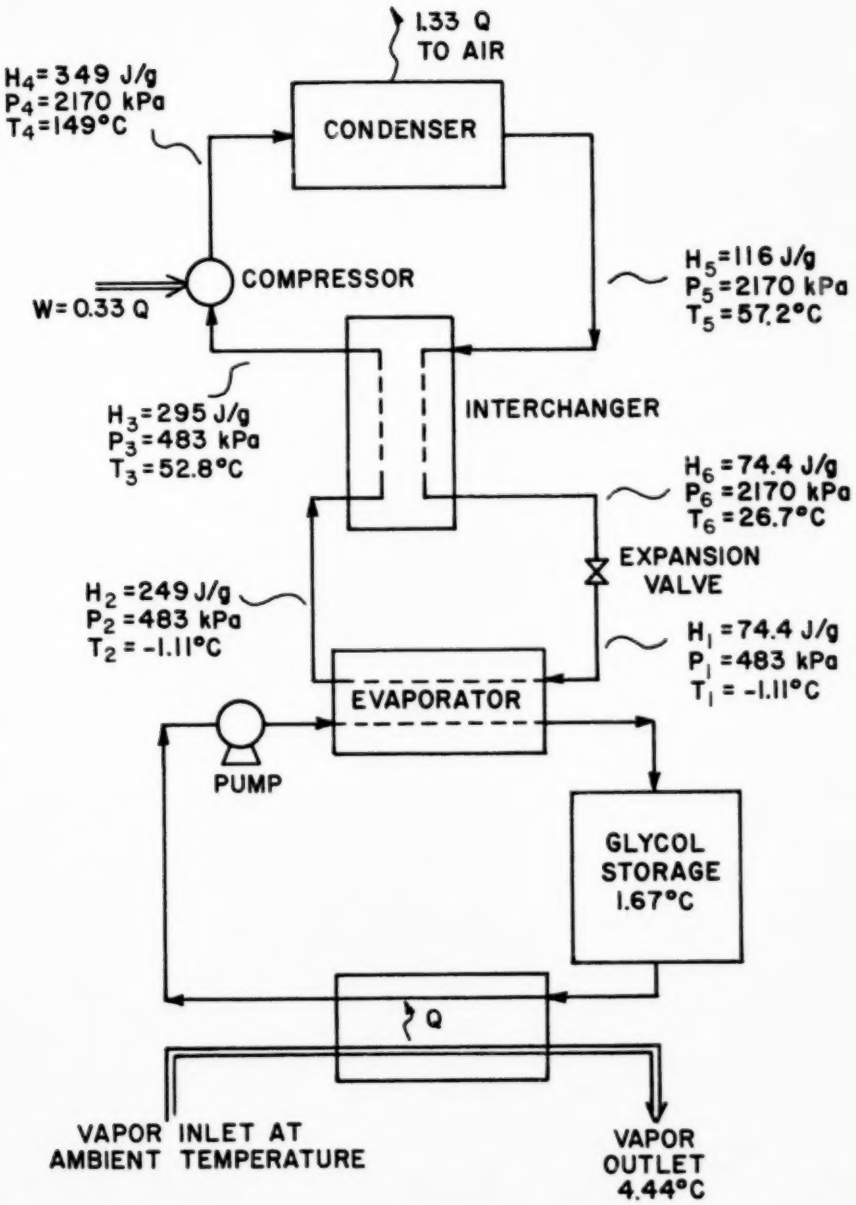

Figure B-1. Precooler refrigeration cycle -- refrigerant enthalpies, pressures, and temperatures used in calculating work requirements.

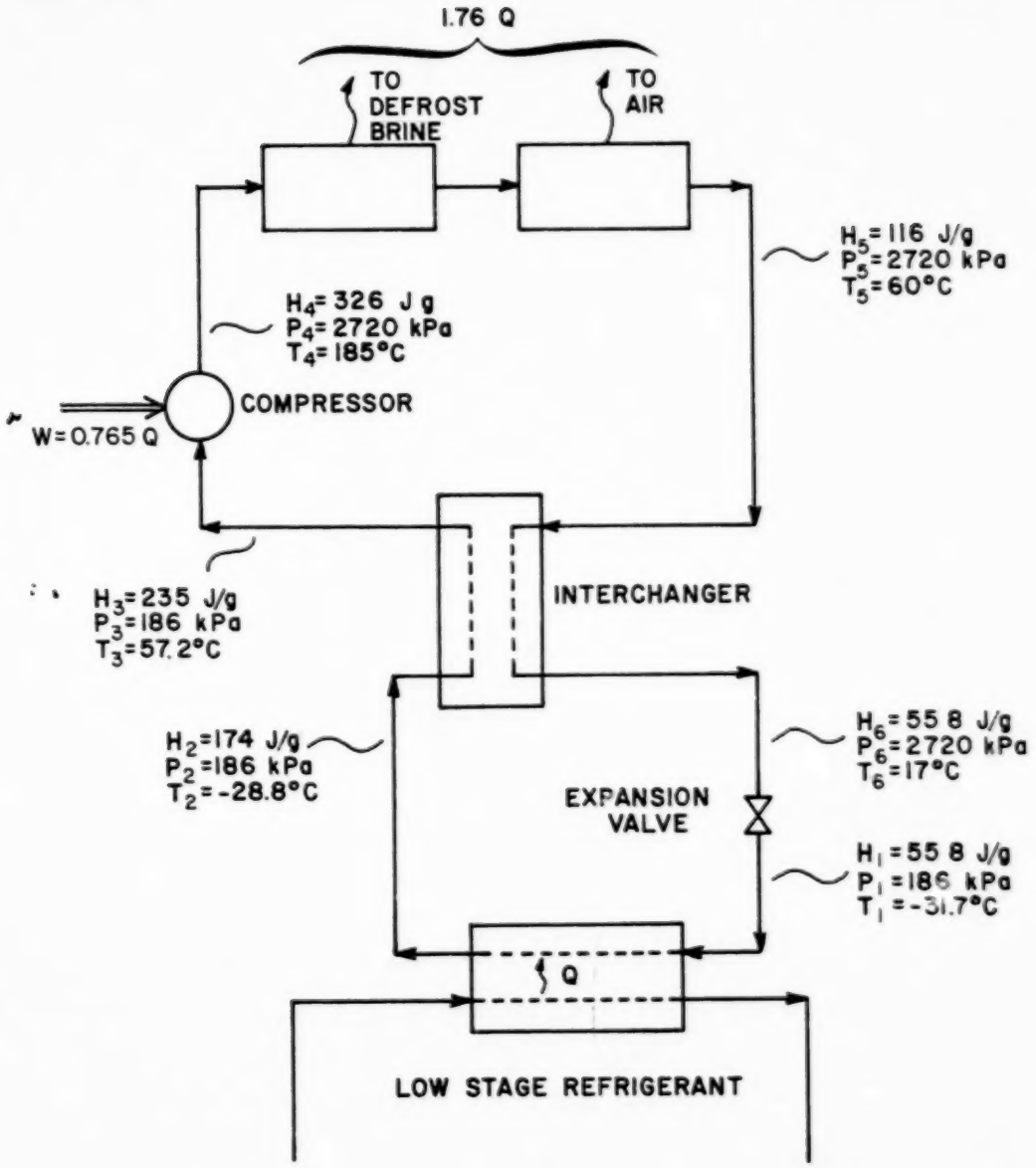

Figure B-2. High stage refrigeration cycle -- refrigerant enthalpies, pressures, and temperatures. Used in calculating work requirements.

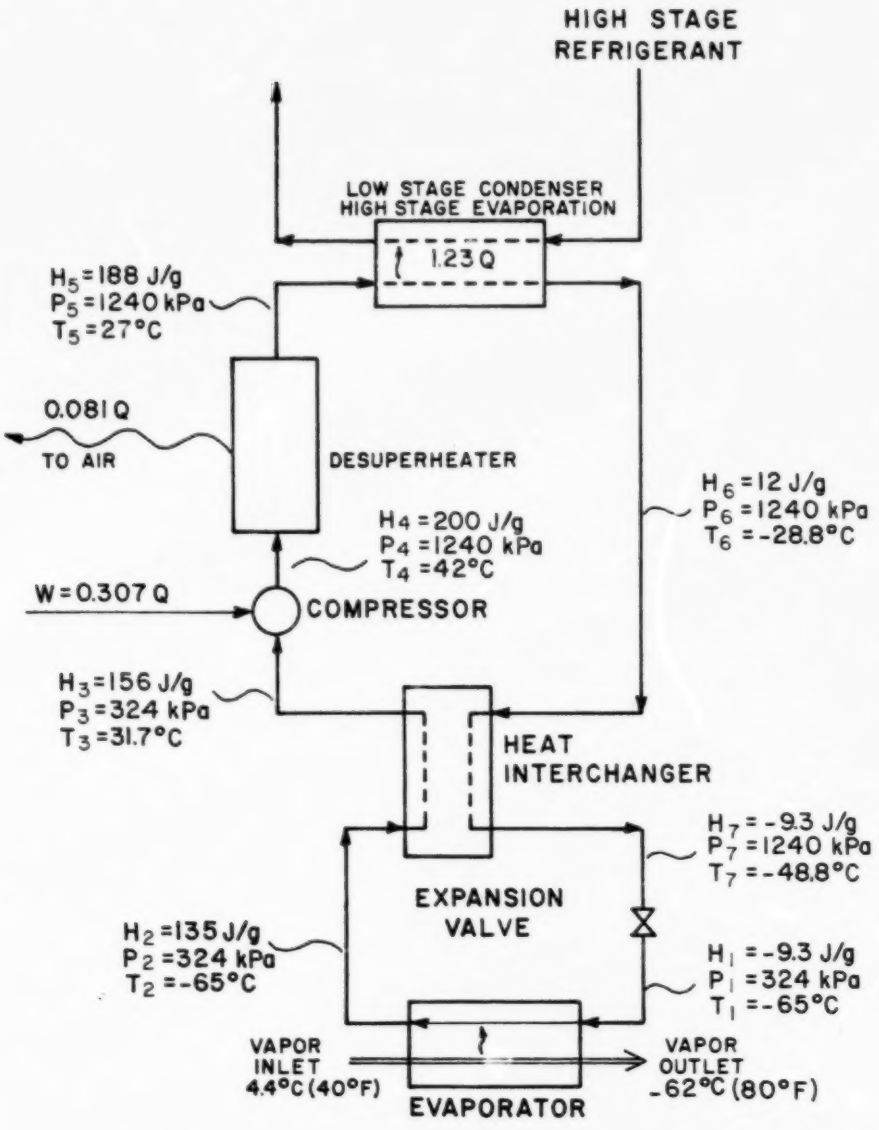

Figure B-3. Low stage refrigeration cycle, outlet temperature = -62°C (-80°F) -- refrigerant enthalpies, pressures, and temperatures used in calculating work requirements.

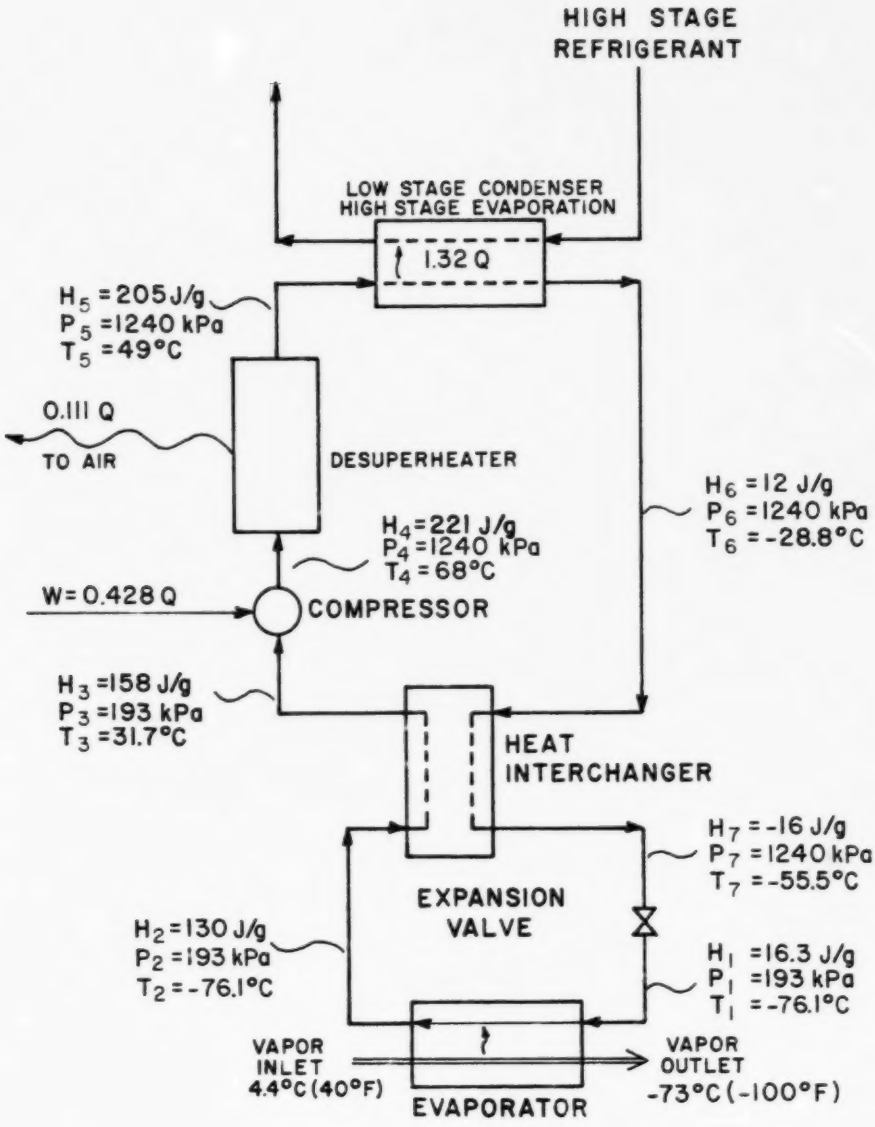

Figure B-4. Low stage refrigeration cycle, outlet temperature = -73°C (-100°F) -- refrigerant enthalpies, pressures, and temperatures used in calculating work requirements.

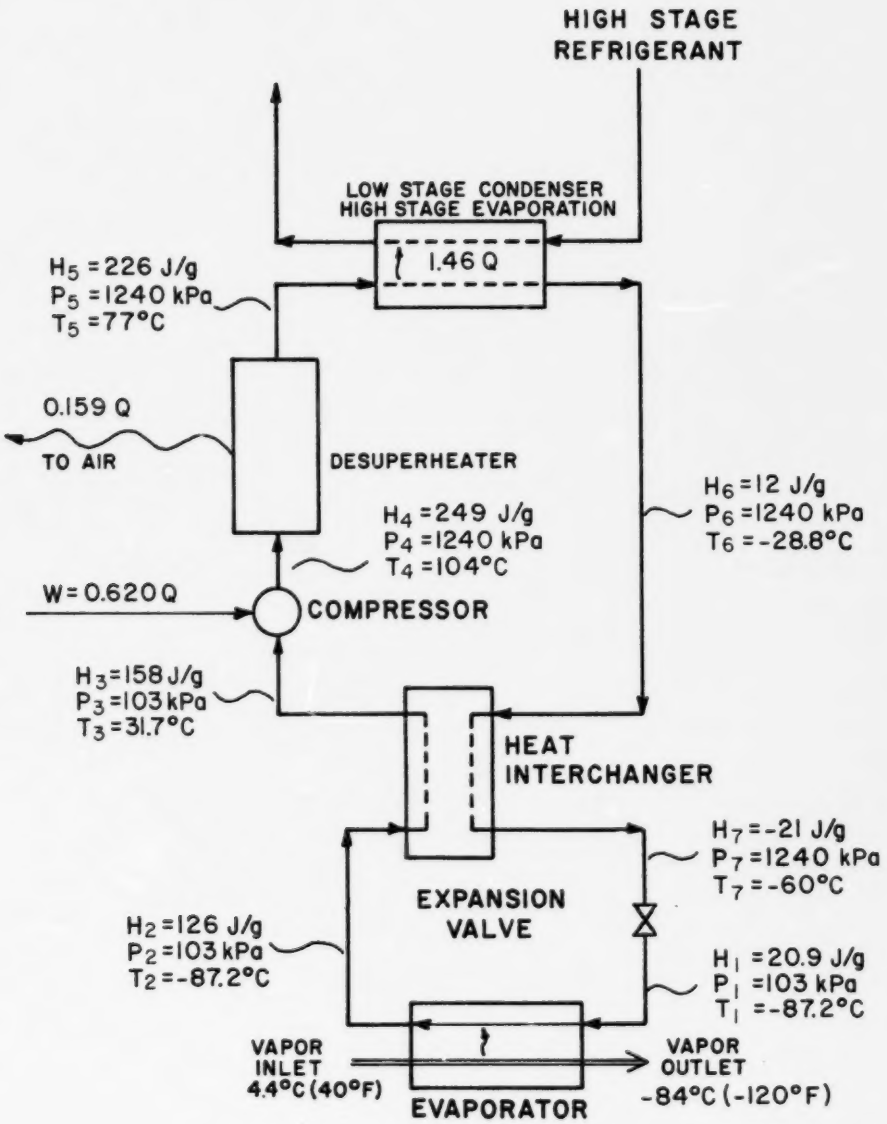

Figure B-5. Low stage refrigeration cycle, outlet temperature = -84°C (-120°F) -- refrigerant enthalpies, pressures, and temperatures used in calculating work requirements.